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BIOLOGICAL AVAILABILITY OF SEDIMENT PHOSPHORUS INPUTS TO THE LOWER GREAT LAKES

by

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16. ABSTRACT

In this study, river water samples were collected from several major tributaries to the Lower Great Lakes during storm runoff events in the spring and early summer of 1980 and 1981. Suspended sediments from these samples were subjected to a chemical fractionation sequence of NaOH-CDB-HCl, as well as algal bioassay analyses of sediment P bioavailability using the Dual Culture Diffusion Apparatus (DCDA) technique of DePinto.

Sediments from several of the bioassay experiments were reconcentrated after the bioassays and resubjected to the chemical fractionation sequence.

Several other forms of P inputs to the Lower Great Lakes were also analyzed for chemical composition and/or bioavailability.

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ABSTRACT

Early efforts to control eutrophication in the Lower Great Lakes focused primarily on the reduction of phosphorus (P) concentrations in wastewater treatment plant effluents discharged to the Lower Lakes basin. Presently, consideration is also being given to the reduction of diffuse (runoff) sources of P through land management practices such as conservation tillage. In assessing the merit of different load reduction programs, it is important to consider the relative bioavailabilities of the various forms of P entering the lakes. In this study, river water samples were collected from several major tributaries to the Lower Great Lakes (Maumee R., Sandusky R., Honey Cr., Cuyahoga R., Genesee R., and Cattaraugus Cr.) during storm runoff events in the spring and early summer of 1980 and 1981. Suspended sediments from these samples were subjected to a chemical fractionation sequence of NaOH-CDB-HCl, as well as algal bioassay analyses of sediment P bioavailability using the Dual Culture Diffusion Apparatus (DCDA) technique of DePinto (1982).

NaOH-extractable P was the largest of the chemical fractions measured for the Ohio tributaries. HCl-P was the largest fraction for New York river sediments, reflecting a geology higher in apatite minerals. The release of sediment P in the presence of P-starved *Selenastrum capricornutum* followed approximately first-order kinetics. The mean percentages of total sediment P (T-Sed-P) determined by the bioassay method to be ultimately available were: Maumee R. - 25.0%; Sandusky R. - 21.4%; Cuyahoga R. - 33.9%; Honey Cr. - 24.9%; Genesee R. - 19.3%; and Cattaraugus Cr. - 7.7%. The chemical fractionation and bioavailability of sediment P showed greater variation between tributaries than among samples from any given tributary. The rate of sediment P release showed relatively little variation between tributaries, and averaged 0.182 day^{-1} for all river sediment samples analyzed.

Sediments from several of the bioassay experiments were reconcentrated and subjected to the chemical fractionation sequence. P released during the bioassays was found to be associated predominately with the reactive NaOH-P fraction (R-NaOH-P). A number of the chemical fractions were strongly correlated with the amount of sediment P ultimately available to *Selenastrum* (P_{ult}). Regression equations of P_{ult} versus R-NaOH-P and non-apatite inorganic P (NAIP = R-NaOH-P + CDB-P) were developed and shown to be significant at the 0.0001 level.

The model expressions currently used to describe P release from suspended sediments in models of Great Lakes trophic status overpredicted the bioassay data for tributary sediments by a

considerable amount after a period of about 7 days. Coefficients were calculated for two different models that more accurately described the bioassay results. In one model, P_{ult} was considered to be released at a single first-order rate, while in the other, P_{ult} was separated into rapidly and slowly released components. Based on the latter model, the rapidly released component comprised the following mean percentages of P_{ult} for the individual tributaries: Maumee R. - 24.3%; Sandusky R. - 29.1%; Cuyahoga R. - 8.6%; Honey Cr. - 17.0%; and Cattaraugus Cr. - 19.4%.

Several other forms of P inputs to the Lower Great Lakes were also analyzed for chemical composition and/or bioavailability. Soluble reactive P in the tributary samples was reduced to very low levels (2-5 µg/l) within 24 hours by P-starved algae in bioassay experiments. Phosphorus in a sewage treatment plant effluent discharged to the Sandusky River was found to accumulate in river bottom sediments in a variety of chemical forms. Other forms of particulate material investigated include Detroit River suspended sediments, Lake Erie bottom sediments, and material from eroding bluffs on the shoreline of Lake Erie.

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ABBREVIATIONS AND SYMBOLS

UNITS

Å	Angstroms
°C	Degrees Centigrade
ft-ca	foot candles
g	Gravitational acceleration
g/l	grams per liter
mg/l	milligrams per liter
μg/l	micrograms per liter
μgP/g sed	micrograms of phosphorus per gram of sediment dry weight
hr	hours
l	liters
ml	milliliters
m	meters
cm	centimeters
mm	millimeters
μm	micrometers (or microns)
nm	nanometers
μM	micromoles per liter
min	minutes
N	Normal (equivalents per liter)

ANALYTICAL CONCENTRATIONS

CDB-P	Sediment P extracted by citrate, dithionite, and bicarbonate reagents in reactive form
HCl-P	Sediment P extracted by hydrochloric acid reagent in reactive form
NAIP	Non-apatite inorganic P (≈ R-NaOH-P + CDB-P)
PP	Particulate phosphorus
NR-NaOH-P	Sediment P extracted by sodium hydroxide reagent in non-reactive form
R-NaOH-P	Sediment P extracted by sodium hydroxide reagent in reactive form
Residual P	Sediment P removed by persulfate digestion after chemical fractionation
SRP	Soluble reactive phosphorus
T-NaOH-P	Total sediment P extracted by sodium hydroxide reagent
TP	Total phosphorus
TPP	Total particulate phosphorus
T-Sed-P	Total sediment phosphorus
TSP	Total soluble phosphorus
TSS or SS	Total suspended solids (>0.45 μm)

DIFFUSION EQUATIONS

A	Open pore area in membrane
D_m	Molecular diffusion coefficient (cm^2/day)
P_o	Initial soluble P level on spiked side of DCDA
P_s	Soluble P level on spiked side of DCDA
P_u	Soluble P level on unspiked side of DCDA
α	Bulk diffusion coefficient (day^{-1})
σ	Membrane thickness

STATISTICAL ANALYSES

C.V.	Coefficient of variation
$H_o: \rho=0$	Null hypothesis
n	Number of observations
r	Correlation coefficient
α	Probability of rejecting a true null hypothesis

PARTICLE SIZE ANALYSIS

A	Coefficient related to total concentration of particulate matter in suspension
BCT	Base channel threshold
CN	Channel number
d_p	Particle diameter
D_{50v}	Volume-weighted median sediment particle diameter
D_{50n}	Number-weighted median sediment particle diameter
N	Particle number
S	Particle surface area
SV_{50}	Median particle settling velocity based on 50% decay in absorbance
SV_{20}	Median particle settling velocity based on 20% decay in absorbance
TF	Threshold factor
V	Particle volume
WW	Window width
β	Power law exponent (unitless)
β_{30}	Power law exponent obtained from Coulter counts with 30 μm aperture

β_{50}	Power law exponent obtained from Coulter counts with 50 μm aperture

DCDA BIOASSAY ANALYSIS

C	Constant of integration
C_1	Soluble P concentration in sediment vessel
C_2	Concentration of algal particulate P in assay vessel
DCDA	Dual culture diffusion apparatus
k_r	First-order release rate of available P(day^{-1})
k_{rr}	First-order release rate for rapidly available component of sediment P (day^{-1})
k_{sr}	First-order release rate for slowly available component of sediment P (day^{-1})
m	Mass of sediments in sediment vessel
P_r	Amount of rapidly-released sediment P
P_{rel}	Amount of P released from sediments at any given time
P_s	Amount of slowly-released sediment P
P_{ult}	Total amount of sediment P ultimately bioavailable
Q_1	Amount of P released from sediments, but remaining in the sediment vessel
Q_2	Amount of P taken up by algae in assay vessel of DCDA
V	Volume of liquid in DCDA vessel
W	Rate of P release from sediments in DCDA (mass/time)

OTHER

AAP	Algal assay procedure
APHA	American Public Health Association
ATP	Adenosine triphosphate
C_o	Initial soluble P concentration (adsorption kinetics)
EDTA	(Ethylenedinitrilo)tetraacetic acid
EPC	Equilibrium phosphorus concentration
ER	Enrichment ratio
K	Constant in adsorption kinetics expression
1/m	Constant in adsorption kinetics expression
M.W.	Molecular weight

NTA	Nitrilotriacetic acid
O.D.	Outside diameter
p.d.	Potential determining
USGS	United States Geological Survey
X	Amount of P adsorbed per unit weight of adsorbent
Δ	Change in a given parameter

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SECTION 1

INTRODUCTION

BACKGROUND

Since the signing of the Great Lakes Water Quality Agreement by the governments of Canada and the United States in April, 1972, an extensive effort has been directed at curbing the problem of eutrophication in the Great Lakes. This attention has been focused primarily on the Lower Lakes (Erie and Ontario), where the most severe problems exist. Reductions in the phosphorus (P) loadings to these lakes are generally considered to be the most effective means of controlling eutrophication. Accordingly, target total phosphorus loads were established based on the reduction of treatment plant effluent phosphorus concentrations to 1.0 mg/l. These were later revised through the use of water quality models to predict the load reductions necessary to achieve the desired water quality for the Great Lakes (Task Group III, 1978). Billions of dollars were committed to improvements in phosphorus removal at wastewater treatment facilities discharging to the Lower Lakes basin. Although municipal loads have decreased considerably, it has now become clear that the revised target loads of 11,000 metric tons/year for Lake Erie and 7,000 metric tons/year for Lake Ontario cannot be met via the present programs. In addition, improvements in the water quality of the lakes resulting from these load reductions have, to date, been disappointing (Sugarman, 1980). Future courses of action being considered include further reductions in municipal treatment plant effluent phosphorus concentrations to 0.5 mg/l and improvement of land management practices (e.g. implementation of conservation tillage programs) in order to reduce diffuse (runoff) sources of phosphorus to the lakes (U.S. Army Corps of Engineers, 1982).

Consideration of these options has caused the utility of target loads based on total P to be questioned. It is now recognized that the relative availability of phosphorus from different sources for supporting algal growth must be carefully evaluated in developing a cost-effective management scheme for the contol of eutrophication (Sonzogni, *et al*., 1982). Nearly 50% of the total P load to Lake Erie and 40% of the Lake Ontario load are from diffuse sources (Chapra and Sonzogni, 1979). A large fraction of this phosphorus is in a sediment-bound form and may, therefore, not be readily available for algal uptake. In fact, studies of several Great Lakes tributaries have indicated that generally 40% or less of suspended sediment total P is potentially bioavailable (Armstrong, *et al*., 1979; Logan, *et al*., 1979). On the other hand, much (often over 70%) of the phosphorus in municipal treatment plant effluents is present in easily assimilable forms (DePinto, et al., 1980; Young, et al., 1982).

To facilitate the evaluation of various programs for eutrophication control, a number of mathematical models have been developed that provide predictions of the water quality improvements that would result from these programs. Several of these models (e.g. Bierman, et al., 1980; DiToro and Connolly, 1980; Thomann, et al., 1975) include explicit distinctions between available and unavailable phosphorus forms. However, the behavior of all particulate P in the water column is assumed to be the same, whether it originates from allochthonous or autochthonous sources. Estimates of the potential bioavailability of particulate P inputs to the Lower Lakes have been made by a variety of methods, including bioassays and chemical extractions. However, the kinetics of conversion of unavailable allochthonous phosphorus to available forms have not been adequately quantified to date. It is possible that particulate material may settle out of the water column before all of its potentially available P is released (Sonzogni, et al., 1982; Logan, et al., 1979). In addition, the rate of phosphorus release from allochthonous particulate material in the water column may differ considerably from the regeneration rate for autochthonous particulate P. Therefore, experimentation designed to characterize the kinetics of phosphorus release from suspended sediments under in-lake conditions could significantly improve the predictive capabilities of trophic status models.

As phosphorus associated with suspended particulate material enters the receiving water environment, it may become available for algal uptake via such mechanisms as desorption, dissolution, and microbial decomposition of organic matter. The degree of particulate P availability depends on the physical, chemical and biological characteristics of the particles and the receiving water. Among the most important factors are the lake's productivity level, soluble inorganic P concentration in the water column, temperature, lake morphometry, hydrology and mixing dynamics, size, shape and density of the particles, and the chemical forms of phosphorus in the particles (Logan, et al., 1979). A more thorough understanding of the relationships between these factors and the bioavailability of particulate P is necessary in order to predict phosphorus release for a wide variety of sediment and receiving water conditions.

OBJECTIVES OF STUDY

The general goal of this research was to obtain information that would permit refinement of mathematical models of lake trophic status through the development of a sediment phosphorus bioavailability submodel. The specific objectives of the experimental program were:

1. to determine the rate and extent of sediment P bioavailability for a variety of tributaries to the Lower Great Lakes under receiving water conditions using a bioassay procedure;

2. to physically and chemically characterize the tributary suspended sediments with respect to factors influencing phosphorus bioavailability;

3. to develop a methodology that may be used to estimate the rate and extent of available P release from suspended sediments based on the characteristics of the sediments;

4. to compare the P bioavailability and chemical characteristics of tributary suspended sediments to other potential sources of sediment P to the Lower Great Lakes.

SCOPE OF WORK

To accomplish the objectives of this study, river water samples were collected from six Lower Great Lakes tributaries (Maumee R., Sandusky R., Cuyahoga R., Honey Cr., Genesee R., and Cattaraugus Cr.) during storm runoff events. Suspended sediments from these samples were concentrated and algal bioassays of sediment phosphorus availability were conducted. The sediments and river water were also subjected to a variety of chemical and physical analyses, including a chemical fractionation sequence for sediment phosphorus and particle size distribution. Kinetic coefficients (rate and amount) for the release of sediment P were determined and correlations between these values and the physical and chemical parameters were examined. This was done in an effort to develop a means of predicting the kinetics of sediment P bioavailability based on a more convenient analytical procedure than the sediment P bioassays.

Several other forms of particulate material from the Lower Lakes basin were characterized in this study as well. These included Sandusky River bottom sediments near a point source of P, Lake Erie bottom sediments, Detroit R. suspended sediments, and shoreline erosion (bluff) sediments.

SECTION 2

CONCLUSIONS

1) The chemical fractionation and bioavailability of P bound to tributary suspended sediments showed little variation among samples from a particular tributary or between the two years of the study (1980 and 1981). Greater disparity was found between tributaries having differences in soil type or land use conditions. Suspended sediments from the Ohio rivers contained higher concentrations of non-apatite inorganic P (NAIP = Reactive NaOH- plus CDB-extractable P) than those from the New York rivers. Sediments transported by the New York rivers contained more apatite P (HCl-extractable) than those from the Ohio rivers.

2) Suspended sediments transported during storm runoff events in Ohio tributaries (Maumee R., Sandusky R., Honey Cr., and Cuyahoga R.) contained higher levels of bioavailable phosphorus than those from New York tributaries (Cattaraugus Cr. and Genesee R.). The mean concentrations of ultimately available sediment P (P_{ult}) measured by DCDA bioassays ranged from 38.8 μgP/g sed. (7.7% of total sediment P) for Cattaraugus Cr. to 449.2 μgP/g sed. (33.9% of total sediment P) for the Cuyahoga R.

3) The release of available phosphorus from tributary suspended sediments in the presence of P-starved *Selenastrum capricornutum* followed approximately first-order kinetics. Release rates (k_r) ranged from 0.043 to 0.266 day^{-1}, and averaged 0.182 day^{-1} for all tributary samples.

4) An expression used to describe P release from water column particulate material in current Great Lakes models (a first-order function of total particulate P) grossly overpredicted the observed release from tributary suspended sediments at times greater than about 7 days. A first-order expression based on the ultimately available fraction of sediment P provided a much more accurate prediction of P release from tributary sediments.

5) A model in which P_{ult} is separated into rapidly released and slowly released components predicted the experimentally observed release slightly more accurately than a single first-order expression based on ultimately available sediment P.

6) Reactive NaOH-extractable P (R-NaOH-P) and NAIP were strongly correlated with P_{ult}. The following regression equations were obtained for P_{ult} versus these two chemical fractions, based on all tributary suspended sediment samples analyzed:

$$P_{ult} = 0.8824 \text{ (R-NaOH-P)} + 17.1 \qquad (r = 0.779)$$

$$P_{ult} = 0.6363 \text{ (NAIP)} - 58.0 \qquad (r = 0.832)$$

7) Phosphorus released from tributary suspended sediments in the presence of P-starved *Selenastrum capricornutum* was predominately associated with the R-NaOH-P fraction. The change measured in the R-NaOH-P fraction during the course of DCDA bioassays averaged over 90% of the P release measured during the bioassays. On the other hand, the change in the CDB-P fraction accounted for under 8% of sediment P release. Changes in the non-reactive NaOH-P and Residual P fractions were closely correlated with the first-order P release rate, k_r.

8) Phosphorus in sediments from eroding bluffs on Lake Erie was predominately associated with apatite, and was completely unavailable to *Selenastrum* over the course of bioassay experiments.

9) The relative contributions of allochthonous and autochthonous material to Lake Erie bottom sediments may vary markedly as a function of location in the lake. In areas receiving substantial autochthonous inputs, the bottom sediments may experience a considerable enrichment in biologically available forms of P. The amount of P released by such sediments upon resuspension may be comparable to, or exceed, that released from tributary suspended sediments (in μgP/g sed).

10) P discharged by a point source (municipal wastewater treatment plant) to the Sandusky R. was found to accumulate in the downstream bottom sediments in a variety of chemical forms. Although all chemically extractable forms of sediment P showed increases at the downstream sampling sites, by far the greatest accumulation occurred in the R-NaOH-P and CDB-P fractions.

SECTION 3

RECOMMENDATIONS

1) The current models of Great Lakes trophic status should be restructured to reflect the distinctly different bioavailability kinetics of particulate P from allochthonous and autochthonous sources.

2) The bioavailability of sediment P transported to the Lower Great Lakes by tributaries (particularly the Detroit River) should be more accurately characterized through additional bioassay and chemical fractionation analyses. Resources could be utilized most efficiently by concentrating the monitoring on areas of differing soil and land use conditions.

3) Regression equations used to estimate the amount and rate of sediment P release based on chemically extractable fractions should be improved by the addition of new data as it becomes available. A better understanding of the mechanisms responsible for these relationships might be gained through analysis of chemical extracts for metals typically active in the binding of P (e.g. Fe, Al, Ca) and/or a measurement of biological activity (e.g. ATP) in the sediments during bioassay experiments.

4) Further experimentation is necessary to check the validity of a two-component model for P release from tributary sediments. More frequent sampling of the reactors during the first week of the bioassays would be required.

5) Studies of the fractionation of P associated with various microorganisms at different stages of growth and decomposition would provide useful insights into relationships between chemically defined fractions of sediment P (e.g. NR-NaOH-P and Residual P) and the release rate of available P.

6) Models of Great Lakes water quality should include expressions describing the resuspension of bottom sediments by wind-induced wave action, coupled with a kinetic expression for the release of P associated with these sediments.

7) Considering the diversity of lake bottom sediments indicated by this study, it is important that the kinetics of sediment P bioavailability be thoroughly characterized at locations where resuspension is likely.

8) Additional study is needed to ascertain the fate of P discharged to Lower Great Lakes tributaries from point sources. In particular, the effect that attachment to bottom and suspended sediments has on the flux of this P to the receiving lake and on its bioavailability should be investigated.

9) The impact of programs aimed at the reduction of diffuse sources of P to the Lower Lakes, such as reduced tillage, should be monitored as these practices are implemented. This would require quantification of the total P flux and the bioavailability of the soluble P and particulate P components before and after implementation of the diffuse source controls.

SECTION 4

REVIEW OF RELATED RESEARCH

INTRODUCTION

Phosphorus has long been recognized as a nutrient essential to the growth of aquatic and terrestrial plants. As a result, extensive information is available in the scientific literature on the chemical forms and dynamics of phosphorus in lakes and soils. However, the biological availability of particulate phosphorus upon entering lakes has only recently been investigated in detail. The objective in this chapter is to summarize the literature that either contributes to the current knowledge of sediment phosphorus availability or indicates a direction for future research on the topic.

PHOSPHORUS TRANSPORT IN TRIBUTARIES

Sediment Transport Mechanisms

The effect that diffuse sources of sediment phosphorus have on a lake's productivity depends to a large extent on the recent history of the particulate material. Important factors include the point of origin of the particles in the watershed or stream and the conditions in the tributary during the period of transport to the lake. Extensive investigations in tributaries to the Great Lakes have provided some useful insights into the transport of phosphorus and suspended solids (U.S. Army Corps of Engineers, 1982).

Most of the total phosphorus transport in streams appears to occur during storm runoff events and in association with suspended sediments (Verhoff, et al., 1979). As stream discharge increases during (or following) a storm event, both total P and suspended solids concentrations typically increase as well (Cahill, et al., 1974; Baker, 1982a). These increases may be largely attributed to two important processes - erosion of soils by surface runoff in the watershed and resuspension of stream bottom sediments.

Rainwater falling on the surface of a watershed moves toward the adjacent stream by two major pathways. During a low-intensity storm, much of the water is able to infiltrate into the soil, and travels laterally to the stream as subsurface flow, or "interflow". This water often contains high concentrations of certain soluble species as a result of prolonged contact with the soil, but is usually low in suspended solids. During high-intensity storms, the infiltration capacity of the soil is exceeded and water flows rapidly over the soil surface toward the stream. This surface runoff water typically contains high concentrations of suspended solids and low concentrations of dissolved substances (Baker, 1982a). A number of studies have shown that the majority of phosphorus in surface runoff is in a sediment-bound form (Harms, et al., 1974; Burwell, et al., 1975; Sharpley and Syers, 1979).

Several authors have also suggested that resuspension of bottom sediments may play an important role in the transport of total phosphorus during storms. Keup (1968) concluded that substantial amounts of phosphorus may be temporarily stored in stream bottom deposits that are subsequently scoured from the channel and rapidly discharged during periods of rising water levels. This transport theory, whereby phosphorus moves from the watershed to the receiving water body in a series of resuspension and deposition steps initiated by storm events, has been termed the Discontinuous Theory (Verhoff and Melfi, 1978). By the opposing view, the Continuous Flow Theory, total phosphorus is considered to be washed from the land, through the river system and into the receiving water body during one storm event.

Verhoff and Melfi (1978) developed a mass balance equation for water and total phosphorus in rivers to investigate the plausibility of these two transport theories. The model results were compared to the characteristics of hydrographs and total phosphorus chemographs observed during storms in four western Ohio tributaries to Lake Erie. These observations revealed that:

-the peak of the total P chemograph almost always precedes the hydrograph peak at the same station;

-the total P concentration declines to its approximate steady-state value before the river discharge; and

-the peak total P concentration is not necessarily higher at the downstream stations than at the upstream stations.

These characteristics could be reproduced only when a resuspension/deposition term was included in the total P mass balance. The results of Verhoff and Melfi (1978) provide strong support for the Discontinuous Theory of total phosphorus transport.

In a subsequent paper, Verhoff, et al. (1979) described a technique for estimating the average distance traveled by total phosphorus passing a given station based on hydrograph and chemograph data. Application of the technique to the Sandusky, Maumee and Cattaraugus Rivers revealed that, where the duration of the hydrograph is short, as in a steeply sloped watershed, the travel distance of total P (and suspended sediments) is also relatively short. However, in the mainstreams of the Sandusky and Maumee Rivers, even rather routine storm events may produce average travel distances on the order of hundreds of miles (Verhoff, et al., 1979).

Based on the large variability in nutrient and sediment loads for storms of equal size, Baker (1982a) has suggested that material export is not limited by the transport capacity of the river, but rather, by the movement of the material from the land surface to the stream system. This is in agreement with the finding presented by Verhoff, et al. (1979) that transport distances tend to be shorter in the upper reaches of a watershed.

Reactions Involving Particulate Phosphorus During Transport

The total phosphorus and sediment transport considerations presented above begin to assume importance in terms of particulate phosphorus bioavailability when one considers the potential reactions involving particulate P during transport in a river system.

Suspended sediments eroded from a surface soil generally have higher particulate phosphorus levels than the soil source. This enrichment in P is attributed to the selective erosion of finer particles, which tend to contain more P (Frink, 1969; Armstrong, et al., 1979). For example, the clay-sized (<4 μm) fraction of suspended sediments collected from the Menomonee River basin was found to account for an average of 77% of sediment dry weight and 88% of total particulate P (Dong, et al., 1983). The effect of this selective erosion is often quantified using a phosphorus enrichment ratio (ER), calculated as the ratio of the P concentration in the suspended sediments to that in the source soil. ER may vary considerably depending upon soil physical and chemical properties, land usage, soil slope and rainfall intensity (Sharpley, 1980).

During fluvial transport, suspended sediments may undergo additional enrichment due to the adsorption of P from solution (Sharpley, et al., 1981; Green, et al., 1978). The adsorption process may also continue after the sediments have been deposited on the stream bottom. Bottom sediments in the vicinity of a point source of phosphorus to the Sandusky River were found to rapidly remove P from solution (Baker, 1980). This phosphorus remained in a sediment-bound form during subsequent runoff events (Baker, 1982b). Also, Dong, et al. (1983) reported sizeable increases in the P content of clay-sized bottom sediments near various sources of P to the Menomonee River.

Green, et al. (1978) reported that bottom sediments from the Maumee River had higher adsorption capacities and higher adsorption energies than suspended solids in the river. It was proposed (by McCallister and Logan, 1978) that chemical changes in eroded soil material following deposition in the stream accounted for the increased adsorption capacity. Formation of amorphous iron oxide precipitates capable of adsorbing additional P was cited as one possibility.

McCallister and Logan (1978) reported equilibrium phosphorus concentration (EPC) values ranging from 8 to 54 µg/l (average = 24 µg/l) for soil clay fractions (the component most likely eroded during a storm event) and bottom sediments from the Maumee River basin. The sediments should tend to adsorb P if soluble levels exceed the EPC and desorb P if the soluble concentration falls below this value. Flux weighted mean soluble reactive phosphorus (SRP) concentrations in the Maumee River were on the order of 100 µg/l for 1975 to 1978 (Baker, 1982a). Therefore, these sediments could be expected to adsorb (rather than desorb) phosphorus during their residence in the river, both when suspended and when deposited on the river bottom. Upon entering the western basin of Lake Erie, where SRP concentrations may remain under 10 µg/l for much of the year (DiToro, 1980), the sediments would tend to desorb P to solution.

Some other processes that could potentially affect the relative distribution of soluble and particulate phosphorus components in streams were mentioned by Keup (1968). These include chemical combination of soluble P with metallic cations to form precipitates and uptake of soluble P by plankton and attached plants. Also, phosphorus assimilated by plants in the stream may be subsequently released through microbial decay of the organic matter (Keup, 1968).

The amounts and chemical forms of the phosphorus present initially in eroded soil and of that accumulated during river transport will have a major influence on the biological availability of particulate P entering the water column of the receiving water. Many investigations have been conducted into the chemical forms of particulate P and their relative mobilities as well as the effects of solution conditions on the uptake or loss of phosphorus by sediments. This work is described in the following sections.

PHOSPHORUS ADSORPTION-DESORPTION STUDIES

Studies of phosphate adsorption characteristics have often been conducted using soils, lake bottom sediments and synthetic minerals as the adsorbent. Since such particles are often chemically similar to suspended and bottom sediments in tributaries, the results of these studies are of interest here as well.

Adsorption Onto Iron and Aluminum Oxide Surfaces

The materials most frequently cited as the major P-sorbing components of soils and aquatic sediments are iron and aluminum oxides. Amorphous complexes of hydrated Fe and Al oxides, in particular, are characterized by numerous hydroxyl groups in surface positions and readily participate in "exchange adsorption" reactions with orthophosphate. These substances have a much higher capacity to adsorb P than crystalline Fe and Al oxides (Williams, et al., 1971a). Based on sorption experiments performed on lake bottom sediments from 14 Wisconsin lakes, Shukla, et al. (1971) postulated that most of the phosphorus adsorbed by both calcareous and noncalcareous sediments was associated with a gel complex of hydrated Fe oxide. The gel complex was also thought to contain small amounts of Al_2O_3, $Si(OH)_4$ and organic matter.

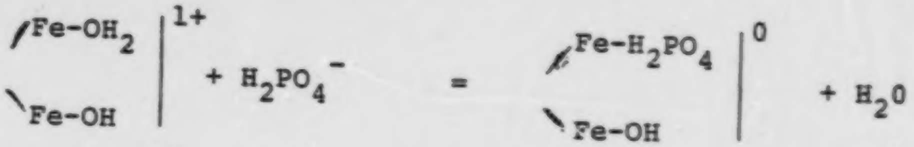
Isotherm Equations--

Adsorption of phosphorus onto Fe and Al oxides frequently follows a "high intensity", or "H-type", isotherm (Ryden, et al., 1977a; Breeuwsma and Lyklema, 1973). That is, plots of P adsorbed per gram of adsorbent versus equilibrium soluble P concentration show a steep rise (next to the ordinate) at low P concentrations. Similar isotherms have been observed for adsorption of phosphorus onto hydrous ferric oxide gel and a variety of soils (Ryden, et al., 1977a), kaolinite, gibbsite (γ-$Al_2O_3 \cdot 3H_2O$) and pseudoboehmite (AlOOH) (Muljadi, et al., 1966a), and hematite (α-Fe_2O_3) (Breeuwsma and Lyklema, 1973).

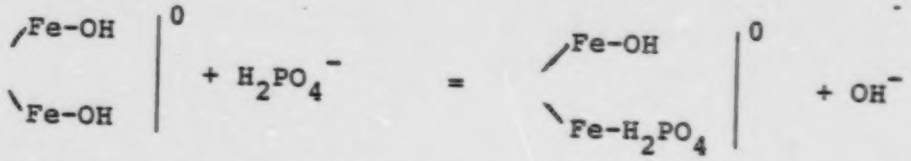
The results of these and other studies have indicated that the mechanism of phosphorus adsorption is not uniform over the entire range of equilibrium P concentrations investigated. Isotherms are often divided into two or more regions of relatively constant adsorption behavior. These regions are then described by separate isotherm equations. Some researchers have combined the Langmuir isotherm with the Freundlich (Kuo and Lotse, 1974) or linear (Muljadi, et al., 1966a) equations, while others (Ryden, et al., 1977a; Syers, et al., 1973) have used a series of Langmuir expressions. An advantage of the latter approach is that consistent estimates of the energy of adsorption may be obtained for all equilibrium P concentrations (Syers, et al., 1973). Chen, et al., (1973a) have indicated that, for P concentrations typical of natural waters ($<10^{-4}$ moles/l), adsorption results can be expected to conform to a Langmuir expression.

Adsorption Mechanisms--

Adsorption at low equilibrium P concentrations is usually dominated by a relatively strong binding of phosphate to the adsorbent. Such high binding energies are characteristic of a chemisorption, or "specific" adsorption, process (Breeuwsma and Lyklema, 1973; Ryden, et al., 1977a). Several authors have proposed mechanisms for the chemisorption of P on the surface of Fe and Al oxides. Adsorption is commonly thought to involve an exchange of phosphate ions for hydroxyl (OH) or protonated hydroxyl (H_2O) groups in the first co-ordination sphere of the metal ions on the oxide surface (Hingston, et al., 1967; Muljadi, et al., 1966a and 1966b; Breeuwsma and Lyklema, 1973; Ryden, et al., 1977a). Although representations of this exchange reaction vary somewhat, they are typically of the form shown in Equations 1 and 2 (from Ryden, et al., 1977a).



$$\left.\begin{matrix}\diagup\text{Fe-OH}_2\\ \diagdown\text{Fe-OH}\end{matrix}\right|^{1+} + H_2PO_4^- = \left.\begin{matrix}\diagup\text{Fe-H}_2\text{PO}_4\\ \diagdown\text{Fe-OH}\end{matrix}\right|^{0} + H_2O \qquad (1)$$



$$\left.\begin{matrix}\diagup\text{Fe-OH}\\ \diagdown\text{Fe-OH}\end{matrix}\right|^{0} + H_2PO_4^- = \left.\begin{matrix}\diagup\text{Fe-OH}\\ \diagdown\text{Fe-H}_2\text{PO}_4\end{matrix}\right|^{0} + OH^- \qquad (2)$$

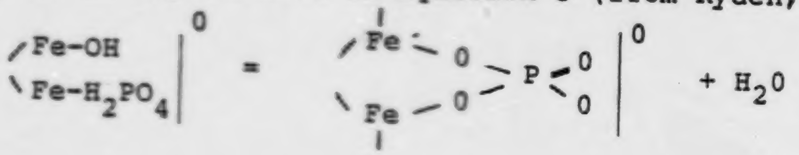
Hsu (1965) suggested that adsorption is a special case of precipitation, and that both processes result from the same chemical force.

Specific adsorption of phosphate on Fe and Al oxides is generally enhanced by the protonation of surface hydroxyl groups due to the resulting formation of positively charged sites. This accounts for the increases in P sorption capacities often observed with decreasing pH. However, there is some disagreement as to the effect of phosphate adsorption on surface charge. Hingston, et al. (1972) proposed two P sorption schemes that would always result in an increase in negative (or a neutralization of positive) charge. On the other hand, the mechanism suggested by Muljadi, et al. (1966a) involves exchange of $H_2PO_4^-$ with OH^- only, and no net change in surface charge.

Using concentrations of sodium (Na) as an indicator of changes in surface charge, Ryden, et al. (1977a) found that, at low levels of P addition (Region I), sorption decreased the surface charge, while at slightly higher levels (Region II), phosphate adsorption caused no change in surface charge. Thus, they concluded that P was adsorbed by both of the mechanisms shown in Equations 1 and 2.

Plots based on a linear form of the Langmuir equation have been used to evaluate the relative binding strength of P for the different regions of adsorption isotherms (e.g. Syers, et al., 1973; Ryden, et al., 1977a). The binding energy is generally found to decrease as the density of P sorbed to the particle surface increases. Ryden, et al. (1977a) found that adsorption in Region I, thought to occur by exchange of $H_2PO_4^-$ for H_2O (Equation 1), was thermodynamically more favorable than Region II adsorption, which was believed to involve exchange with OH^- (Equation 2). They indicated that additional Region I adsorption accounted for most of the observed increases in P sorption capacity (of iron oxides and soils) resulting from decreases in pH. In addition, this study revealed remarkable similarities in the free energies of adsorption between a laboratory preparation of ferric oxide gel and several soils of varying chemical composition. Thus, it is likely that P is sorbed to all of these particles by the same mechanism (Ryden, et al., 1977a).

A number of researchers have attributed the strong binding of phosphate on Fe and Al oxide surfaces at low equilibrium P concentrations to the formation of a binuclear complex such as that shown in Figure 1 (Atkinson, et al., 1972; Kafkafi, et al., 1967; Hingston, et al., 1974). Infrared spectroscopy results obtained by Parfitt, et al. (1975) indicated that this complex was the principal mode of phosphate adsorption onto the surfaces of several synthetic iron oxides. The formation of a binuclear complex is consistent with the surface charge data collected by Ryden, et al. (1977a). This could occur by a condensation reaction involving singly co-ordinated phosphate at the oxide surface as represented in Equation 3 (from Ryden, et al., 1977a).



$$\left.\begin{matrix}\diagup\text{Fe-OH}\\ \diagdown\text{Fe-H}_2\text{PO}_4\end{matrix}\right|^{0} = \left.\begin{matrix}\diagup\text{Fe}-\text{O}\\ \diagdown\text{Fe}-\text{O}\end{matrix}\!\!>\!\text{P}\!\begin{matrix}\text{O}\\ \text{O}\end{matrix}\right|^{0} + H_2O \qquad (3)$$

Hingston, et al. (1974) have characterized phosphate adsorption as a ligand exchange reaction and designated the left-hand and right-hand sides of Equation 3 as monodentate and bidentate configurations, respectively.

Specific adsorption of P on Fe and Al oxide surfaces has been found to be largely irreversible with respect to phosphate concentration (Hingston, et al., 1974; Kafkafi, et al., 1967), although desorption may be induced by increases in pH (Muljadi, et al., 1966a). Limited desorption has also been reported for soils (Ryden, et al., 1977a) as well as river bottom (Oloya and Logan, 1980) and suspended (Green, et al., 1978) sediments at low levels of surface coverage by phosphate. However, evidence of the mobility of adsorbed P was presented by Li, et al. (1972), who found that 19 to 34% of the total inorganic P in lake bottom sediments was exchangeable (with ^{32}P). The observed

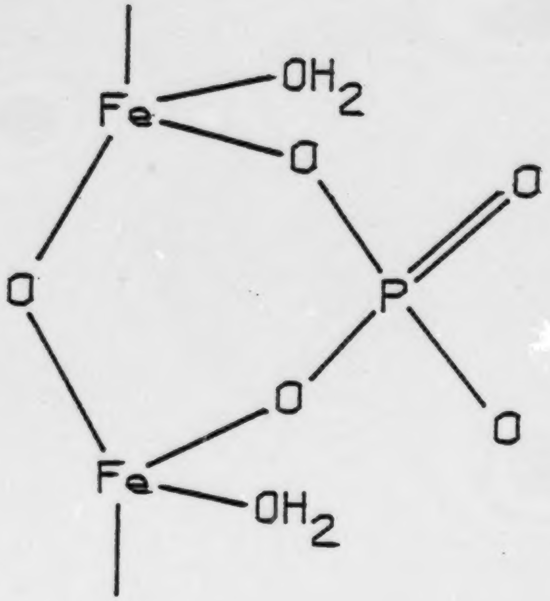

Fe
OH2
O
O
O
P
O
O
Fe
OH2

Figure 1. Binuclear complex(from Hingston, et. al., 1974).

irreversibility is often attributed to the presence of the highly stable binuclear complex discussed above (Atkinson, et al., 1972; Hingston, et al., 1974).

Ryden, et al. (1977a) suggested that adsorption of phosphate onto soils and Fe oxide gel was essentially irreversible at equilibrium soluble P concentrations up to 25 µM (775 µgP/l), while Muljadi, et al. (1966a) saw evidence of irreversibility at concentrations up to 100 µM (3100 µgP/l) for adsorption onto Al oxides and kaolinite. Phosphate adsorption at higher levels of added P is generally dominated by a weaker, more reversible binding mechanism. The increase in P sorption with increasing ionic strength observed in this region of the isotherms implies that phosphate acts as a potential-determining (p.d.) ion (Ryden, et al., 1977a; Breeuwsma and Lyklema, 1973). This adsorption is more physical, or "non-specific", in nature than adsorption at lower equilibrium P concentrations. A p.d. sorption mechanism is consistent with the linear portions of isotherms observed at high P concentrations (Muljadi, et al., 1966a; Breeuwsma and Lyklema, 1973) since no absolute sorption maximum would be expected (Ryden, et al., 1977a).

Parameters Affecting Phosphate Adsorption--

Some of the parameters that may affect P sorption on Fe and Al oxides as well as soil and sediment particles have been mentioned briefly above. The most important factors include the pH and ionic composition of the solution and the surface area of the adsorbent. At equilibrium P concentrations up to about 1 mg/l, decreases in pH have been shown to result in increases in the adsorption of P onto iron oxide surfaces (e.g. hematite and goethite) over a wide pH range (2-12). Although adsorption also exhibits a general increase with decreasing pH at higher P concentrations, the opposite effect has been observed over narrow pH ranges in the vicinity of $pH=pK_2$ (=7.2 for phosphate) (Breeuwsma and Lyklema, 1973). A somewhat different behavior has been reported for P adsorption onto several Al oxides and clays. Adsorption of P from solution onto these materials increased as pH was decreased, reaching a maximum at about pH 4-5. However, further decreases in pH caused abrupt reductions in the amounts of P adsorbed (Chen, et al., 1973a; Edzwald, et al., 1976; Muljadi, et al., 1966a). Similar trends were seen for a wide range of phosphorus concentrations. Edzwald, et al. (1976) noticed a different pH dependency for the adsorption of phosphate onto montmorillonite. They found a roughly linear increase in P sorption with increasing pH (between 2 and 10). This was attributed to reaction of exchangeable calcium on the clay with P to form an insoluble calcium phosphate phase.

The presence of certain ions in the surrounding solution (or "support medium") has been shown to affect the adsorption of phosphate on a variety of Fe and Al oxides and soils. Chen, *et al*. (1973a) found that some cations (Ca^{2+}, La^{2+}, and a cationic polyelectrolyte) increased P adsorption onto alumina (γ-Al_2O_3) and kaolinite for pH>4. They indicated that cations increase phosphate adsorption by reducing the repulsive force between a negative surface and phosphate ions. However, since other cations (Ni^{2+}, Co^{2+}, and Mg^{2+}) did not influence adsorption perceptibly, it is not likely that the observed effects may be explained entirely by electrostatic interactions. Helyar, *et al*. (1976) reported that divalent cations with ionic radii near 1.0 Å (e.g. Ca, Cd, and Sr) increased the adsorption of phosphate by gibbsite, while larger or smaller ions (e.g. Mg, Zn, Na, and K) showed little effect. These authors proposed the formation of a surface complex composed of adsorbed P and a divalent cation, and suggested that ion size is more important than electronegativity in complex formation. Other studies have shown that, while phosphate adsorption generally increases with increasing ionic strength of the support medium, the introduction of some cations (e.g. Ca^{2+}) results in an additional enhancement of P adsorption beyond that expected on the basis of ionic strength alone (Robarge and Corey, 1979; Ryden and Syers, 1975). However, for phosphate adsorption onto soils, at least, it appears that the ionic strength and the dominant cation often affect only the kinetics of P removal from solution by the adsorbent. Ryden and Syers (1975) found that, for low levels of P addition, where chemisorption dominates overall sorption, differences due to ionic strength and cation effects were eliminated at equilibrium. At higher phosphate concentrations (>30 μM), on the other hand, differences in adsorption similar to those mentioned above were maintained at equilibrium (Ryden, *et al*., 1977b).

The influence of various anions in the surrounding solution on phosphate adsorption by clays and Al oxides has also been investigated. Chen, *et al*. (1973a) reported that sorption of P onto kaolinite and alumina decreased in the presence of certain anions (e.g. F^-, humic acid) for pH<6, while others (e.g. HCO_3^-, $SiO(OH)_3^-$) showed little influence on adsorption. The same study also demonstrated a decrease in phosphate sorption over a wider pH range (pH<8) upon the addition of complexing agents such as tartrate, EDTA, and citrate. The effects of Cl^- and SO_4^{2-} additions on the adsorption of P by clays was used by Edzwald, *et al*. (1976) to assess the role of ion exchange reactions in phosphate sorption. These anions caused no decrease in the

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amounts of P adsorbed, indicating that sorption is not driven by a purely electrostatic mechanism.

The phosphate sorption capacity of any material depends to a large extent on the surface area of the particles. Amorphous Fe oxides and hydroxides have a considerably greater surface area than substances with more crystalline structures, such as goethite, hematite, gibbsite, clays and soils, and also exhibit much higher P sorption capacities (Parfitt, et al., 1975; Ryden, et al., 1977a; Muljadi, et al., 1966a). Bottom sediments in lakes and rivers may be exposed to conditions (water saturation and fluctuating redox potential) that favor the formation of amorphous hydrated metal oxides. It has been proposed that coatings of these materials can result in substantial increases in the P sorption capacity of aquatic sediments (McCallister and Logan, 1978; Shukla, et al., 1971; Williams, et al., 1971a).

Adsorption Onto Calcium Carbonate

Although the sorption of phosphate onto aquatic sediments has been largely attributed to Fe and Al oxides on the particle surfaces, there is evidence that calcite ($CaCO_3$) may also contribute to the P sorption capacity of some sediments (Green, et al., 1978; Wentz and Lee, 1969). Green, et al. (1978) found that the calcite content of suspended river sediments was positively correlated with native total sediment P and negatively correlated with adsorption energy. They concluded that, while P can be adsorbed by calcite, the binding force is weak and P may be easily desorbed. Other studies, conducted on lake bottom sediments (Shukla, et al., 1971) and on soils and river bottom sediments (McCallister and Logan, 1978) have shown negative correlations between $CaCO_3$ content and phosphate sorption for calcareous as well as noncalcareous sediments.

Experiments have been conducted to characterize the adsorption of phosphate onto commercially prepared calcium carbonate. The isotherms consisted of a wide range of equilibrium P concentrations (0 to 2500 μgP/l, or more) where results conformed to the Langmuir equation, followed by a range corresponding to calcium phosphate precipitation (Kuo and Lotse, 1972; Cole, et al., 1953). However, even at the upper end of the Langmuir portion of these isotherms, the amounts of P adsorbed were well below 100 μgP/g $CaCO_3$. This is small compared to the total sediment P concentrations (mostly >1000 μgP/g sediments) reported by Green, et al. (1978). Thus, if calcite is to make a significant contribution to the P sorption capacity of sediments, it must certainly do so via a different mechanism than was operative in these studies.

Kinetics of Phosphate Adsorption and Desorption

In assessing the impact of sediment-bound phosphorus loads on receiving waters, the kinetics of interactions between P and particle surfaces must be considered. An investigation of phosphate adsorption onto alumina and kaolinite revealed a rapid adsorption step for 12-24 hr, followed by a slower, first-order rate process extending over the next 60 days (Chen, et al., 1973b). Kuo and Lotse (1974) characterized the kinetics of both adsorption and desorption of phosphate by lake sediments. Adsorption was described by Equation 4, which was developed from the Freundlich equation.

$$X = K\ C_o\ t^{1/m} \tag{4}$$

where:
X = Amount adsorbed (μgP/g sediment)
C = Initial phosphorus concentration (ppm)
t = Reaction time
and, K and 1/m are constants.

The same authors reported that, although desorption of native sediment P was negligible except in the presence of NaOH or EDTA, significant percentages of freshly adsorbed P were rapidly desorbed in accordance with a kinetic expression similar to Equation 4. This is contrary to the results of Li, et al. (1972), who indicated that native P in lake bottom sediments and freshly sorbed P showed roughly the same degree of exchangeability with ^{32}P, and that exchange kinetics could be resolved into three first-order reactions. In this study, the majority (mean = 76%) of exchangeable P was found to participate in a rapid reaction, at an average rate of 34.7 hr^{-1}. Atkinson, et al. (1972) concluded that the rate of ^{32}P exchange at the surface of goethite was first-order with respect to the concentration of a Fe(III)-phosphate surface complex, and independent of the solution P concentration. In another study, conducted on river sediments and soils, two different pools of desorbable native P were identified - one exhibiting a rapid release independent of desorption time and another obeying first-order kinetics (Oloya and Logan, 1980). A technique for estimating the amount of phosphate that would be desorbed as the solution P concentration approached zero as a function of desorption period was presented by Barrow (1979) and applied to P desorption from a soil.

The kinetics of phosphate interactions with calcium carbonate have also been investigated. Phosphate adsorption onto the surface of calcite was described by second-order kinetic expressions in two separate studies (Kuo and Lotse, 1972; Griffin and Jurinak, 1974). Kuo and Lotse (1972) reported that about 80% of phosphate adsorption by $CaCO_3$ was completed in 10 seconds.

The formation of a calcium phosphate precipitate on the surface of calcite at high soluble P concentrations was found to conform to first-order kinetics. The desorption process (studied in the presence of an anion exchange resin) could be described by two simultaneous first-order expressions. It was proposed that one reaction involved a rapid (rate = 0.049 hr^{-1}) dissolution of surface-nucleated calcium phosphate minerals, while the other involved a slower (rate = 2.4×10^{-4} hr^{-1}) desorption of phosphate from calcite surface sites (Griffin and Jurinak, 1974).

The studies of phosphate adsorption and desorption discussed in this section may provide a better theoretical understanding of the processes affecting the accumulation of phosphorus by sediments during transport and the biological availability of sediment-bound P upon entering the receiving water. However, much of this work was conducted under conditions substantially different from the aquatic environments to which sediments are typically exposed. Thus, it is not possible to obtain accurate quantitative estimates of sediment P bioavailability based on information acquired from these investigations. For example, whereas minimal desorption of both native and freshly sorbed P has been observed when Fe or Al oxide, soil or sediment particles are placed in P-free ionic media (Hingston, et al., 1974; Ryden, et al., 1977a; Oloya and Logan, 1980), sediments incubated in the presence of an active P-starved algal culture are often found to release over 20% of native sediment P (Cowen and Lee, 1976a; Williams, et al., 1980a; Dorich, et al., 1980). Recently, techniques have been proposed for quantitatively characterizing the bioavailability of sediment-bound P. The evolution of these techniques is reviewed in the following sections.

CHEMICAL FRACTIONATION OF SEDIMENT PHOSPHORUS

The development of techniques for the characterization of sediment-bound phosphorus can be largely attributed to researchers in the field of soil science. A variety of chemical extraction procedures have been used to estimate the availability of soil phosphorus to agricultural crops. These procedures usually remove P by one or more of the following processes (Logan, 1978):

1. Displacement of soluble P held in soil pores;
2. Exchange of $H_2PO_4^-$ adsorbed to soil surfaces with another anion;
3. Dissolution or hydrolysis of soil P complexes.

Several extraction methods originally designed for use on soils have been applied to lake and river sediments as well. These include the Bray P1 (0.03 M NH_4F + 0.025 N HCl) extraction (Bray and Kurtz, 1945), the procedure of Olsen, et al. (1954) (0.5 M $NaHCO_3$), and extraction with acid ammonium oxalate (Saunders, 1965). Applications of these techniques to aquatic sediments have been reported by McCallister and Logan (1978), Romkens and Nelson (1974), and Williams, et al. (1971a), respectively, as well as others. However, sediment P bioavailability has more commonly been estimated using the procedure recommended by Chang and Jackson (1957), or a modification thereof.

Chang and Jackson (1957) first proposed a scheme for the fractionation of sediment phosphorus into discrete chemical forms. They suggested that treatment of soils with an extraction sequence of NH_4F, NaOH, H_2SO_4, citrate-dithionite reagent and NH_4F again would selectively remove aluminum phosphate, iron phosphate, calcium phosphate, occluded iron phosphate and occluded aluminum phosphate, respectively. The occluded phosphates were thought to be chemically similar to the iron and aluminum phosphates extracted by NH_4F and NaOH, but protected from removal by iron oxide coatings that were insoluble in these extractants. The authors also indicated that the NaOH step often removed considerable organic phosphorus. This fraction was eliminated from the extract solution (prior to analysis) by acidification (to induce flocculation) followed by centrifugation.

The fractionation sequence proposed by Chang and Jackson (1957) was based on the view that aluminum- and iron-bound phosphate in soils was predominately in the form of discrete crystalline phases such as variscite ($AlPO_4$) and strengite ($FePO_4$). This view, referred to as the "discrete phosphate" theory (Williams and Walker, 1969), has been questioned in papers by Bache (1963 and 1964), Bauwin and Tyner (1957), and Hsu (1964). Williams, et al. (1971a) indicated that no direct observations of discrete Al of Fe phosphates had been recorded in unfertilized soils or lake sediments. A more common belief today (called the "dispersed phosphate" theory) is that much of the inorganic P in soils consists of phosphate ions chemisorbed onto reactive surfaces such as iron and aluminum oxides or hydrous oxides and amorphous alumino-silicates ("non-occluded" P), or retained within the matrices of these materials or various soil minerals ("occluded" P) (Williams and Walker, 1969; Logan, 1978). A certain amount of soil or sediment P may also be present in discrete phosphate minerals such as apatite ("discrete" P) or in organic forms such as esters of phosphoric acid ("organic" P) (Williams, et al., 1971a). Although the "discrete phosphate" theory is no longer widely accepted, the work of Chang and Jackson (1957) has served as a basis for additional research.

Some problems with the Chang and Jackson (1957) fractionation scheme were pointed out and some modifications suggested by Williams, et al. (1971b and 1971c). The results of extractions on noncalcareous lake bottom sediments indicated that the P removed by NH_4F was largely present in association with Fe rather than Al components of the sediment (Williams, et al., 1971c). In addition, calcium fluoride, formed during NH_4F extraction of calcareous materials, was found to "resorb" inorganic phosphorus released during the same extraction (Williams, et al., 1971b). The authors suggested, therefore, that the NH_4F extraction could not be used to distinguish between Al- and Fe-bound P, and proposed that this step be eliminated. However, they indicated that this would not eliminate the problem of resorption because $CaCO_3$ can sorb inorganic phosphorus released during extraction with NaOH. In fact, the P extracted from calcareous sediments by citrate-dithionite-bicarbonate (CDB) reagent was thought to consist largely of P resorbed by $CaCO_3$ during a preceding NaOH extraction step. As a result of this study, in which five different fractionation schemes were evaluated, a sequence of NaOH, CDB, and HCl was recommended. The sum of the NaOH- and CDB-extractable P fractions was said to provide an estimate of Fe- plus Al-bound P, while treatment with HCl removed P present as apatite.

In subsequent fractionation studies on Lake Erie bottom sediments, Williams, et al. (1976a and 1976b) reversed the order of the NaOH and CDB steps, presumably in order to avoid resorption of P onto $CaCO_3$. The sum of CDB-P and reactive NaOH-extractable P (R-NaOH-P) was termed non-apatite inorganic P (NAIP) and that removed in the HCl step was labeled apatite P. These authors reported that the extra P extracted by the NaOH step in this procedure was seldom greater than 4% of the CDB-P value. They suggested, therefore, that a scheme employing only CDB and HCl could provide an adequate separation of NAIP from apatite P.

Recent studies aimed at determining which forms of phosphorus are released by the various extraction reagents (Williams, et al., 1980b; Hieltjes and Lijklema, 1980) have been conducted using discrete phosphate minerals of known compositions. This work has revealed still another potential problem with the common fractionation schemes. While most calcium-bound phosphates and apatite minerals were not solubilized appreciably by treatment with NaOH or CDB, a large portion of the P associated with hydroxy-apatite ($Ca_5(PO_4)_3OH$) was extracted by the CDB step. Thus, in some cases, it may not be possible to separate NAIP from apatite P in sediments.

In both soils and aquatic sediments, organic P may constitute a significant fraction (typically 10-60%) of total sediment P (Frink, 1969; Syers and Walker 1969; Sommers, et al., 1972; McCallister and Logan, 1978). Organic P in soils or sediments is often measured using the method of Mehta, et al. (1954), which involves successive extractions with concentrated HCl, 0.5 N NaOH at room temperature, and 0.5 N NaOH at 90° C. The extract solutions are combined, and organic P calculated as the difference between the measured total P and inorganic (reactive) P concentrations. Sommers, et al. (1972) proposed a similar sequence of extractions, but analyzed each extract separately to gain insights into the forms of organic P present. They suggested that HCl would extract low molecular weight organic P compounds that are similar to inorganic P in their nature of chemical association with sediments, while the NaOH fractions consist largely of ill-defined humic-associated P complexes in sediments. The cold NaOH step removed most (60-86%) of the total organic P in lake bottom sediments, while the HCl step extracted only 6-17% (Sommers, et al., 1972).

Based on a review of the phosphorus fractionation literature, it appears that, for certain types of soils or sediments, an extraction sequence of NaOH-CDB-HCl may provide a meaningful separation of sediment P fractions. Sediments containing little $CaCO_3$ or hydroxy-apatite should release mostly P sorbed to surfaces of iron and aluminum oxides and hydrous oxides and organic P during the NaOH step. The CDB extraction should then remove mostly P occluded within the matrices of iron and aluminum oxides and minerals, with the HCl step solubilizing predominately apatite P. Unfortunately, the mineral composition of river suspended sediment or lake bottom sediment samples is often complex and difficult to determine. Thus, the exact origin of P removed by different steps in the fractionation schemes is frequently unknown. Data obtained from sequential extractions may be useful, nevertheless, as an indicator of the strength with which P is bound to the sediments. Since the sequence proceeds from the most selective extractant to the least selective, the P removed in the earlier steps of the procedure is likely to be the most weakly bound to the sediments, and thus, the most environmentally reactive (Logan, 1978).

Analyses of the total and/or extractable concentrations of certain metals (especially Fe, Al, and Ca) associated with P in sediments may be used to suggest the likely origin of extractable P fractions. For example, Williams, et al. (1971a) found a strong statistical correlation between Fe and P extracted from lake bottom sediments by CDB. Metals analyses on the sediments might also indicate the likelihood of encountering problems such as resorption onto $CaCO_3$ or release of P from hydroxy-apatite by CDB during the fractionation scheme.

ESTIMATION OF SEDIMENT P BIOAVAILABILITY BY CHEMICAL METHODS

The original phosphorus fractionation schemes were used by soil chemists to study the reactions of phosphorus fertilizers in soils. More recently, chemical extractions have also been used to estimate the bioavailability of phosphorus associated with sediments in aquatic systems. Estimates have also been obtained using other chemical techniques, such as equilibration of sediments with a P-free solution or with an ion exchange resin, exchange with ^{32}P, and incubation with chloroform.

Armstrong, et al. (1971) suggested that the potential mobility of sediment inorganic P could best be interpreted in terms of the amounts of non-occluded, occluded, and apatite P present. They considered interstitial inorganic P (extractable by neutral salts such as NaCl or NH_4Cl) to be chemically mobile and that present in occluded forms (solubilized by reductants such as dithionite) or as apatite (HCl-extractable) to be essentially immobile. Non-occluded inorganic P (NaOH-extractable) was considered to be in equilibrium with inorganic P in solution and thus was labeled "potentially mobile".

In subsequent work on sediments transported by five major tributaries to the Great Lakes, Armstrong, et al. (1979) estimated the availability of sediment P by two different chemical methods - extraction with 0.1 N NaOH and equilibration with an anion exchange resin (Dowex 1X-8). The mean estimates of available phosphorus for the individual rivers ranged from 14 to 37% of the total particulate P by the NaOH extraction method and from 7 to 17% by the resin method.

Armstrong, et al. (1979) also separated river sediments into three size fractions (0.2-2 µm, 2-20 µm, and >20 µm) and analyzed each for total and "available" P. They found that total, resin-exchangeable, and NaOH-extractable phosphorus concentrations (per gram of sediment dry weight) generally increased as the particle size decreased. Since efforts to reduce sediment loads to the Great Lakes (by methods such as no-till farming) are likely to favor removal of larger particles from runoff, this finding suggests that the fractional reduction in the available P load will probably be somewhat less than the reduction in sediment load.

The available P concentrations of suspended sediments from over 30 tributaries in the Lake Erie basin have been estimated by Logan (1978) using the NaOH-CDB-HCl extraction sequence of Williams, et al. (1971b). In this study, R-NaOH-P was considered to be rapidly available for algal uptake, while the R-NaOH + CDB fraction was assumed to represent the total potentially available sediment P. R-NaOH-P was found to be on the order of 30-40% of total sediment inorganic P for Michigan and Ohio streams, but averaged only 14% for New York streams. (R-NaOH + CDB)-P ranged from an average of 42.5% of total sediment inorganic P for New York streams to an average of 88.6% for eastern Ohio streams.

The soluble reactive component of NaOH-extractable phosphorus (R-NaOH-P) was used by Baker (1982b) to estimate the bioavailability of P associated with suspended sediments in over 400 samples from ten sampling sites in the Sandusky River basin. The R-NaOH-P fraction made up a relatively constant percentage of the total sediment phosphorus (T-Sed-P) for medium to high flow conditions and suspended solids concentrations. R-NaOH-P was also approximately the same at both mainstream and tributary stations, with averages ranging from 20.8 to 24.9% of T-Sed-P for the individual sampling sites. Although point sources of P to the Sandusky River have been found to move rapidly into the stream sediments (Baker, 1982a), no significant increases in R-NaOH-P downstream of point sources was detected under the sampling and analytical conditions employed by Baker (1982b). Reddy (1980), however, reported sizeable increases in NaOH-extractable P in Genesee River bottom sediments due to point source discharges.

Wildung and Schmidt (1973) measured the release of P from lake bottom sediments by two different dialysis techniques. One method involved the equilibration of sediments, enclosed in cellulose acetate dialysis tubing, with water. The other involved placement of sediment and water in two different glass half-cells separated by a membrane filter with a pore size of 0.45 um. Comparison of results using the dialysis methods and measurements of P release in the presence of an anion exchange resin led the authors to conclude that the presence of a continuous P sink increased the release of P from sediments considerably. Another resin method was used by Huettl, et al. (1979) to predict the availability of phosphorus in simulated runoff suspensions. A cation exchange resin was saturated with hydroxy-aluminum and equilibrated with the sediment suspensions. The phosphorus adsorbed was considered to be the algal-available fraction, and ranged from 20 to 40% of the total inorganic P.

The availability of particulate phosphorus in Lake Memphremagog (Quebec-Vermont) and five of its tributaries was measured by treating unfiltered samples with chloroform and monitoring increases in soluble P (Peters, 1981). Chloroform stops biological uptake by killing cells, but does not inhibit enzymatic breakdown of organic P substrates. The average P release for the individual tributaries was reported to be between 17 and 66% of the total particulate P. The availability of P contained in three other fractions (soluble P, small molecular weight P and large molecular weight P) was derived from particulate P availability estimates using the relative exchangeability of these P fractions for $^{32}PO_4$ (Peters, 1981). Using a similar technique, Carignan and Kalff (1979) found the amount of isotopically exchangeable P in lake sediment to be a good measure of the P available to macrophytes.

Using chemical extraction procedures, it is possible to obtain relatively quick and reproducible estimates of sediment P availability. However, there are also serious disadvantages associated with the use of these methods (Logan, et al., 1979). In most cases, no attempt is made to simulate the receiving water conditions under which release of P from suspended sediments will occur. Also, the chemical methods supply little or no information regarding the rate at which sediment P becomes available. In order to predict the amount of phosphorus that is released for algal uptake before sediments settle out of the water column, it is necessary to characterize the kinetics of sediment P release under receiving water conditions. Another drawback of the chemical methods for estimating sediment P availability is that often only inorganic P is considered (Logan, et al., 1979). However, the results of Armstrong, et al. (1979) indicate that organic P may constitute a sizeable fraction of the total sediment P in river suspended sediments. Rodel, et al. (1977) reported that certain organic P compounds sorbed to lake sediments were released via hydrolysis reactions, although rates were slower than for soluble organic P. Organic P may, therefore, make a significant contribution to bioavailable sediment P. These difficulties can be overcome by the use of bioassay methods to measure the rate and extent of sediment P bioavailability.

BIOASSAY MEASUREMENT OF SEDIMENT P AVAILABILITY

Sediment P bioassay studies conducted to date have generally involved the culturing of algae in a suspension of river or lake sediments where the sediments provide the only source of P to the algae and all other nutrients are in excess supply. Following an incubation period, either the algal phosphorus content or algal biomass (employing a P:biomass ratio for conversion) is used to estimate the amount of sediment P that has become available (Logan, et al., 1979). Some investigators have applied one or more chemical methods in conjunction with bioassay measurements of sediment P availability in an effort to find a correlation that would allow prediction of biossay results by a less time-consuming method.

One of the first bioassay measurements of phosphorus availability in aquatic sediments was performed by Golterman, et al. (1969) on bottom muds from two Dutch lakes. They monitored the increase in cell number of Scenedesmus incubated in the presence of lake muds as the only source of P. The apparent phosphorus release was then calculated by comparing the log growth rates with those observed for known orthophosphate concentrations. By this method, algal uptake of P was estimated at 7% of the total sediment P in one lake and about 29% in the other. The authors also found that the decrease in the sum of NaOH- and H_2SO_4-extractable P forms corresponded fairly well with the algal P uptake calculated using a mean cell P content of 9.1×10^{-8} µgP/cell.

In a later study, Golterman (1976) found that the phosphorus fraction removed from sediments by three successive extractions with 0.01 M NaNTA was similar to that removed by Scenedesmus. He also found that the sequential CDB and NaOH extractions proposed by Williams, et al. (1976a) removed slightly more phosphorus than the three NTA extractions. A later study of lake bottom sediments conducted by Allan and Williams (1978) revealed a good correlation between the CDB and NTA extractions. As a result, the authors suggested that the P fraction extracted by CDB alone could be considered available.

Fitzgerald (1970) investigated the growth of Selenastrum and Cladophora sp. exposed to lake bottom muds (in dialysis tubes) as the only source of phosphorus using absorbance at 750 nm as a biomass indicator. Although significant algal growth was caused by soluble P or sediments spiked with soluble P in dialysis tubing, sediments alone resulted in no growth response. However, Hegemann, et al. (1982) indicated that bioassays in which soil samples were enclosed in dialysis tubing showed much lower P release than those in which the soil was in direct contact with the algal culture. It is possible that, since the contents of the dialysis tubes were not continuously mixed in these studies, diffusion of soluble P to the surrounding culture was slow, providing an opportunity for released P to resorb to the sediments.

The availability of particulate P in urban runoff from Madison, Wisconsin was measured by Cowen and Lee (1976a) using a bioassay procedure. The test alga, Selenastrum capricornutum was incubated for a period of 19-22 days in assay flasks containing AAP medium minus P and runoff sediments. Available P was then determined by comparing cell counts to a standard curve of 18-day cell counts versus initial orthophosphate concentration. Available P measured by this procedure ranged from 8 to 55% of the total particulate P (TPP), with a mean of 30%. The

NaOH-extractable fraction, which ranged from 22 to 27%, corresponded most closely with the bioassay results. Exchangeable P (anion exchange resin-extractable), which ranged from 13 to 17% of particulate P, slightly underestimated the algal-available fraction, while an acid extraction, which removed from 33 to 46%, overestimated bioavailability.

Cowen and Lee (1976b) also used the procedure described above to measure the availability of P in sediments transported to Lake Ontario by the Genesee River. They found that 6% or less of the sediment P was available based on the growth of *Selenastrum*. In this case, both the NaOH-extractable (11-28% of TPP) and resin-extractable (6-31% of TPP) fractions overestimated the bioassay results.

Williams, *et al*. (1980a) cultured several forms of sedimentary material from the Lower Great Lakes basin with P-starved *Scenedesmus quadricauda* and used a standard curve of cell counts versus initial orthophosphate added to calculate the availability of sediment P. The fractionation scheme outlined by Williams, *et al*. (1976a) was also applied to the sediments. By comparing the chemical and biological measurements, the authors concluded that apatite P and organic P in the sediments did not support algal growth, while from 38 to 83% of the nonapatite inorganic P became available during 12-day incubations.

There are several problems associated with the use of algal biomass changes, rather than actual P uptake, to assess sediment P availability (Logan, *et al*., 1979; Hegemann, *et al*., 1982). Most of the problems stem from the fact that algae are capable of taking up P in excess of their immediate metabolic needs, which can result in a highly variable P:biomass stochiometry. In addition, it is quite possible that algae would respond differently in terms of growth rate and cell P quota to a high initial spike of orthophosphate (as used in developing standard curves) than to a gradual release (typical of a sediment P source) of the same amount of P (Logan, *et al*., 1979). Further complications could arise if the P uptake and growth response in the synthetic medium used for the standard curve and/or sediment bioassays differs from the response under receiving water conditions.

Sagher (1976) found evidence of inaccuracies associated with the use of constant P:biomass ratios to interpret sediment P bioassay data. He compared algal uptake calculated from *Selenastrum* cell numbers with a measurement in which NaOH and HCl extractions were used to monitor the decrease in total inorganic P (assumed to be incorporated into organic forms within algal cells) in the sediment-algae suspensions. The estimate of sediment P availability obtained by the chemical method (37% of sediment inorganic P) was much more realistic than that obtained using cell numbers (91% of sediment inorganic P). The bioassay results obtained by Sagher (1976) corresponded very closely with estimates of sediment P availability based on a resin exchange procedure (Huettl, et al., 1979).

In bioassay experiments on sediments suspended in runoff water, Dorich, et al. (1980) used a method similar to that of Sagher (1976). They suspended sediments in a nutrient medium, inoculated them with *Selenastrum* and incubated them for two weeks. The amount of phosphorus assimilated by the algal cells was then calculated by comparing the results of sequential extractions (NH_4F-NaOH-HCl) applied before and after incubation to determine the decrease in sediment inorganic P. They reported that an average of about 20% of the total sediment P was immobilized by the algae. Dorich, et al. (1980) also conducted bioassay experiments using both sterilized and nonsterile sediment samples in order to determine the role of native microorganisms in the removal of P from sediments. They found that the sterilization process did not greatly affect the measured release of sediment P and suggested, therefore, that bacteria, protozoa and microflora are not essential for releasing P to algae. It should be noted, however, that the chemical measurements of availability by Dorich, et al. (1980) and Sagher (1976) would not detect the mineralization and release of sediment organic P, which could be mediated by these organisms.

The relative bioavailabilities of P from various sources (including river water, Grand River suspended sediments, shoreline bluff material and tertiary treated sewage effluent) to the Great Lakes were estimated by Millard, et al. (1979) using lake column simulators. Bioavailability was measured by monitoring the response of five different algal biomass indicators to continuous inputs of the P sources to the columns, and comparing these responses to that for an equivalent input of orthophosphate. The authors indicated that P in the sewage effluent was essentially all available for algal uptake, while shoreline erosion (bluff) material contained negligible amounts of available P. Difficulties encountered in interpreting the results for Grand River suspended sediments again demonstrated the problems associated with the use of algal biomass to estimate the availability of P sources.

Most of the bioassay studies discussed above were conducted using a single incubation period between 12 and 28 days in duration and an indirect measurement of algal uptake of P. Recently, bioassay methods have been developed which allow periodic harvesting of the algae and direct measurement of algal P uptake. The release of P from one acid and one neutral soil was found to continue for up to 112 days when the algal culture was replaced with a fresh inoculum every 14 days (Hegemann, et al., 1982). In another study, Verhoff, et al. (1978) investigated the removal of phosphorus from Lake Erie tributary sediments by the indigenous phytoplankton population. Their procedure involved periodically decanting the water from the incubation tanks, leaving most of the river sediments at the bottom of the tank. Following retention of an aliquot for total P analysis and removal of the algae by centrifugation, the water was returned to the tank and the incubation continued. A mass balance performed on total phosphorus and total inorganic solids allowed calculation of the rate of conversion to available P. The authors concluded that a linear availability rate of 0.2-0.4% of total sediment P per day could be expected. This slow rate of release over long time periods suggests that the rate of P release is more important than the ultimate bioavailability (Logan, *et al.*, 1979). However, few reliable measurements of sediment P release rates are presently available.

DePinto (1982) has recently proposed an experimental apparatus, called a Dual Culture Diffusion Apparatus (DCDA), for investigating both the rate and extent of sediment P bioavailability. The DCDA consists of two glass vessels that are clamped together and separated by a polycarbonate membrane with a 0.4 μm pore size. By placing a sediment suspension in one vessel and a P-starved algal culture in the other, mixing of the algae and sediment particles is prevented while exchange of soluble substances between the vessels is possible. Since the P-starved algal culture maintains the soluble P level in the algal (or "assay") vessel near zero, phosphorus released from the sediments diffuses across the membrane where it is taken up by the algae. The contents of the assay side are removed periodically for analysis of the P uptake and are replaced with a fresh P-starved culture. The kinetics of sediment P release are then quantified by performing a mass balance on phosphorus on both sides of the DCDA. This technique allows a reasonable reproduction of the receiving water conditions under which P release from suspended sediments actually takes place as well as a direct measurement of algal uptake of released P. The procedure of DePinto (1982) was used for all bioassays of algal-available P in this study.

SECTION 5

EXPERIMENTAL METHODS

SAMPLE COLLECTION

In order to characterize the bioavailability of sediment P inputs to the Lower Great Lakes, river water samples were collected from five major tributaries to the lakes during storm runoff events. The rivers selected (Maumee, Sandusky, Cuyahoga, Cattaraugus (South Branch), and Genesee) represent a variety of soil types (i.e. geochemistries and textures) and land use conditions (Logan, 1978; U.S. Army Corps of Engineers, 1982). The location of these tributaries within the Lower Lakes basin is shown in Figure 2.

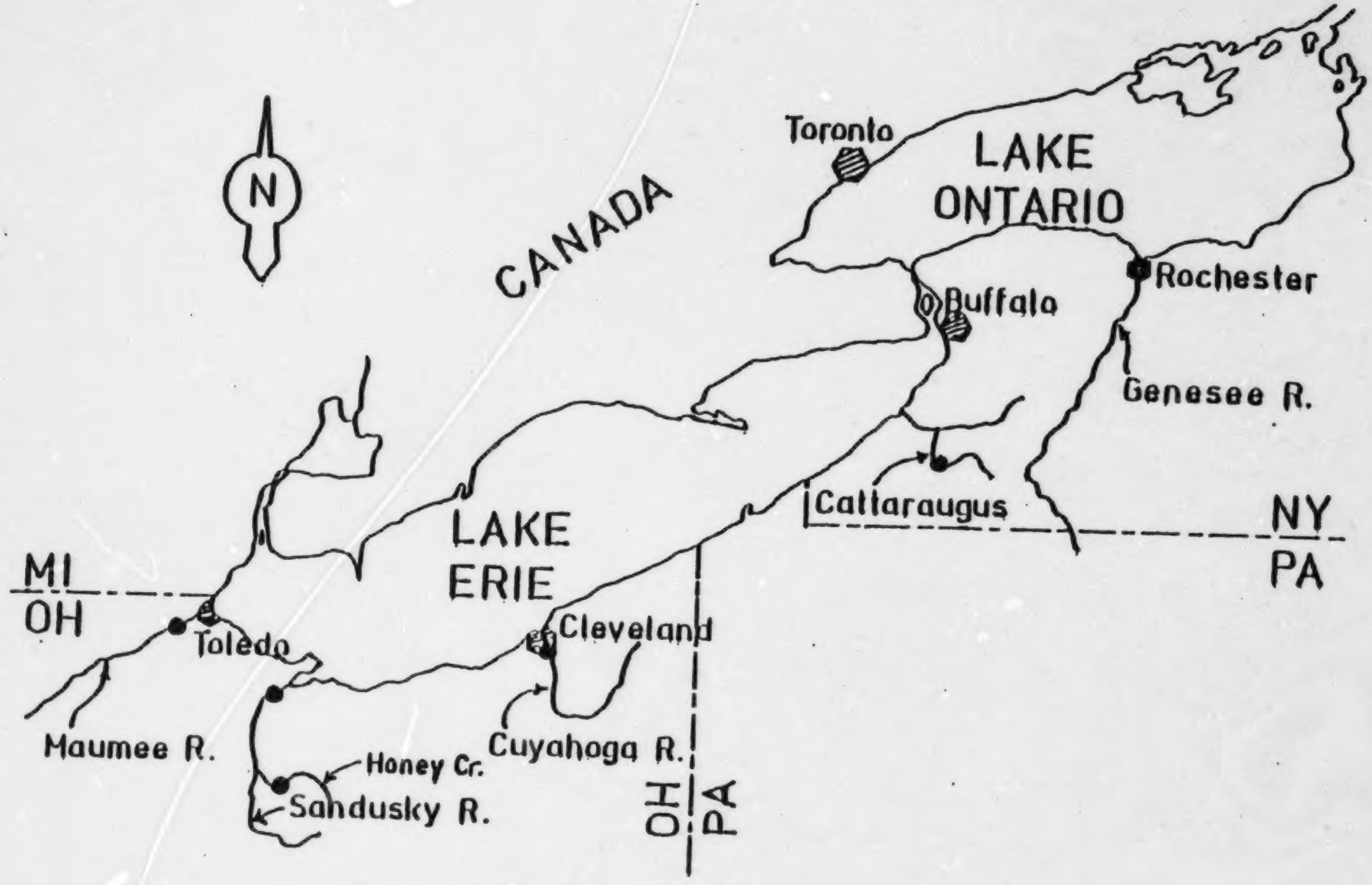
Sampling for the first year of this project was conducted on all five rivers during the late winter and spring (March - June) of 1980. Grab samples were taken at mid-depth in the rivers at sampling stations located as close as possible to the mouth without influence from the lake. The locations of the stations are listed in Table 1 along with the USGS identification numbers and the field personnel who conducted the sampling. All sampling sites were located at or near USGS guaging stations, so a record of flow at the time of sampling could be obtained.

During the second year of the study, a more diversified sampling program was undertaken. The individual components of the program were as follows:

1. The event-oriented sampling of spring 1980 (i.e. one sample per storm event) was continued on the Maumee and Cuyahoga Rivers during the spring of 1981;

2. River water samples were collected from the Sandusky River at various times during each of four different storm runoff events in the spring of 1981. Four to six samples were taken per event in order to study trends in available P discharge.

3. Samples were also collected from Honey Creek, a tributary to the Sandusky, during high flow periods. The Honey Creek watershed was the site of a three year (1979-1981) pilot program to demonstrate and promote the use of conservation tillage for the reduction of soil and phosphorus losses. The present study should provide



CANADA
Toronto
LAKE ONTARIO
Rochester
Buffalo
Genesee R.
Cattaraugus
NY
PA
LAKE ERIE
MI
OH
Toledo
Cleveland
Maumee R.
Honey Cr.
Sandusky R.
Cuyahoga R.
OH
PA
N

Figure 2. Location of tributary sampling sites.

TABLE 1. TRIBUTARY SAMPLING STATIONS AND SAMPLE COLLECTORS

Tributary	Sampling location	USGS sampling station I.D. no.	Sample collector
Ohio Rivers:			
Cuyahoga River	Independence, Ohio	04208000	Water Quality Lab
Maumee River	Waterville, Ohio	04193490	Heidelberg College
Sandusky River	Fremont, Ohio	04198000	Tiffin, Ohio
Honey Creek	Melmore, Ohio	04197100	
New York Rivers:			
Cattaraugus Creek (South Branch)	Otto, New York	04213490	U.S. Army Corps of Engineers Buffalo, New York
Genesee River	Rochester, New York		William Prytherzh Rochester Gas and Electric Co. Rochester, N.Y.

background information on sediment P availability that may be useful in assessing the effectiveness of such land management practices at a future date.

4. Six longitudinally-spaced bottom sediment samples were taken from the Sandusky River in August, 1981. Three of the sites were upstream from the Bucyrus, Ohio, sewage treatment plant, and three were downstream.

5. Suspended sediment samples were obtained from four locations on a transect across the Detroit River north of Grosse Ile, Michigan.

6. Four bottom sediment samples were collected from the western basin of Lake Erie - two near the Toledo, Ohio, water intake and two near the Monroe, Michigan, water intake.

7. Three shoreline erosion (bluff) samples were obtained - two from Lake Erie (at Rondeau Park and Port Stanley, Ontario) and one from Lake Superior (near Bardon Creek, Ontario).

A summary of the locations and dates of collection for all samples is presented in Table 2.

SAMPLE HANDLING AND PREPARATION

For each of the runoff event samples listed in Table 2, an 8 to 10 liter volume of river water was transferred on site to a polyethylene cubitainer. The cubitainers were then cooled to 4 °C as soon as possible, packed with frozen ice packs in large insulated transportation containers, and shipped to Potsdam, NY, via the quickest carrier service available. Upon receipt at Clarkson College, the samples were stored at 4 °C until preparation and analysis.

The contents of the cubitainers were mixed thoroughly, and a one liter aliquot of each sample was retained for physical and chemical characterization of the unfiltered river water. The remainder of the sample was filtered under positive pressure through a 0.45 µm pore diameter Nuclepore nitrocellulose membrane. A one liter aliquot of the filtrate was also saved for analysis. The non-filterable residue was removed from the membrane using a stainless steel spatula, and resuspended in a phosphorus-free, synthetic medium (see foonote in Table 6) at a suspended solids concentration of about 10 g/l. This sediment concentrate was stored at 4 °C until its subsequent use in particulate P fractionation and algal bioassay experiments. Studies showed that the release of inorganic P from sediments

TABLE 2. DATES AND LOCATIONS OF SAMPLE COLLECTION

Sample number	River	Date collected	Sample number	River	Date collected
(A) Tributary Samples - All samples collected at stations listed in TABLE 1.					
1	Cuyahoga	3/8/80	28	Sandusky	4/15/81
2	Sandusky	3/9/80	29	Cuyahoga	4/15/81
3	Genesee	3/20/80	30	Sandusky	4/18/81
4	Cuyahoga	3/22/80	31	Sandusky	4/13/81
5	Maumee	3/20/80	32	Honey Creek	4/14/81
6	Cattaraugus	3/23/80	33	Honey Creek	4/30/81
7	Sandusky	3/22/80	34	Sandusky	4/30/81
8	Maumee	3/25/80	35	Sandusky	5/1/81
9	Cattaraugus	4/6/80	36	Sandusky	5/2/81
10	Cattaraugus	4/14/80	37	Sandusky	5/3/81
11	Sandusky	4/15/80	38A	Sandusky	5/14/81
12	Cuyahoga	4/15/80	38	Sandusky	5/15/81
13	Maumee	4/15/80	39	Sandusky	5/16/81
14	Cuyahoga	5/28/80	40	Sandusky	5/17/81
15	Maumee	5/28/80	41	Maumee	5/5/81
16	Sandusky	5/27/80	42	Maumee	5/11/81
17	Maumee	5/20/80	43	Honey Creek	6/10/81
18	Sandusky	5/19/80	44	Sandusky	6/9/81
19	Maumee	6/3/80	45	Sandusky	6/10/81
20	Sandusky	6/5/80	46	Sandusky	6/11/81
21	Maumee	6/10/80	47	Sandusky	6/12/81
22	Cattaraugus	6/20/80	48	Honey Creek	6/14/81
23	Cattaraugus	6/20/80	49	Sandusky	6/14/81
24	Sandusky	6/2/80	50	Maumee	6/16/81
25	Sandusky	6/9/80	51	Sandusky	6/15/81
26	Sandusky	4/14/81	52	Sandusky	6/16/81
27	Maumee	4/14/81			

(continued)

TABLE 2 (continued)

Sample number	Name of sampling site	Direction from treatment plant	Distance from treatment plant	Latitude N	Longitude W
(B) Sandusky River Bottom Sediments - All samples collected on 8/13/81.					
1	Locustgrove	upstream	9 miles	40°50'10"	82°52'30"
2	McCurdy	upstream	7	40°49'50"	82°54'00"
3	Weiss	upstream	3	40°49'00"	82°56'20"
4	Kestetter	downstream	0.5	40°48'30"	83°00'20"
5	Shupp	downstream	5	40°46'20"	83°03'00"
6	10d	downstream	10	40°44'30"	83°06'30"

(C) Detroit River Suspended Sediments - Collected during Summer, 1981.

Locations:

Four points along a transect of the river north of Grosse Ile, Michigan. Samples were labeled as follows:

Fox Island
Trenton Channel
Livingston Channel
Amherst Channel

(D) Lake Erie Bottom Sediments

Sampling Locations	Date Collected
Toledo, Ohio Water Intake (2 samples)	10/1/80
Monroe, Michigan Water Intake (2 samples)	11/10/80

(E) Shoreline Erosion (Bluff) Sediments

Sampling Location	Date Collected
Rondeau Park, Ontario - Lake Erie	9/16/80
Port Stanley, Ontario - Lake Erie	9/16/80
2 miles west of Bardon Creek, Ontario - Lake Superior	9/11/80

stored at 4 °C as a concentrate for prolonged periods (up to 6 months) averaged less than 2% of the total sediment P.

The Detroit River suspended sediments were collected by personnel from the EPA Large Lakes Research Lab at Grosse Ile, Michigan, via pressure filtration of river water at the EPA lab. Filter membranes (0.45 µm pore size) containing the sediments were placed in plastic screw-cap bottles and refrigerated prior to transport to Potsdam. Due to the low quantities of sediments on the membranes, it was necessary to composite sediments from all Detroit River sites into one sediment concentrate for analysis.

The bottom sediments from the Sandusky River and Lake Erie, and the shoreline erosion (bluff) samples were all grab samples that were shipped to Clarkson College in insulated coolers. Sediment concentrates were prepared by resuspending several representative fine-grained portions of each sample in the P-free media. Two sediment concentrates were made from each of the Lake Erie bottom sediment and bluff samples to check the likelihood of sample inhomogeneities.

ANALYTICAL PROGRAM

A summary of the analytical program conducted on tributary samples is presented in Figure 3. Analyses performed on unfiltered river water samples included total suspended solids >0.45 µm (SS), total phosphorus (TP), and particle size distribution, while filtrates were analyzed for total soluble (i.e. filterable) P (TSP) and soluble reactive P (SRP). During the first year of the project, suspended solids removed by a 20 µm nylon mesh and pH were also determined on several of the river water samples. In addition, a number of measurements of alkalinity and soluble P bioavailability (by bioassay) were made on the filtrates. During the second year, analyses of sediment particle sinking velocities were conducted on many of the unfiltered tributary samples as part of a related research project. Total suspended solids (SS) analyses were performed on the sediment concentrates to allow calculation of the volumes necessary for chemical fractionation and algal bioassay studies. Sediments were reconcentrated following bioassay experiments on several of the 1981 samples, and subjected to the chemical fractionation sequence. The total phosphorus (TP) concentration of sediment concentrates was also measured. The ratio TP/SS for sediment concentrates is equal to the total sediment phosphorus (T-Sed-P) concentration in µgP/g sediment. The procedures used in performing the various physical, chemical, and biological analyses mentioned above are listed, with the corresponding references, in Table 3. Most of these are also described in more detail in the next section.

For bottom sediment (L. Erie and Sandusky R.), bluff, and

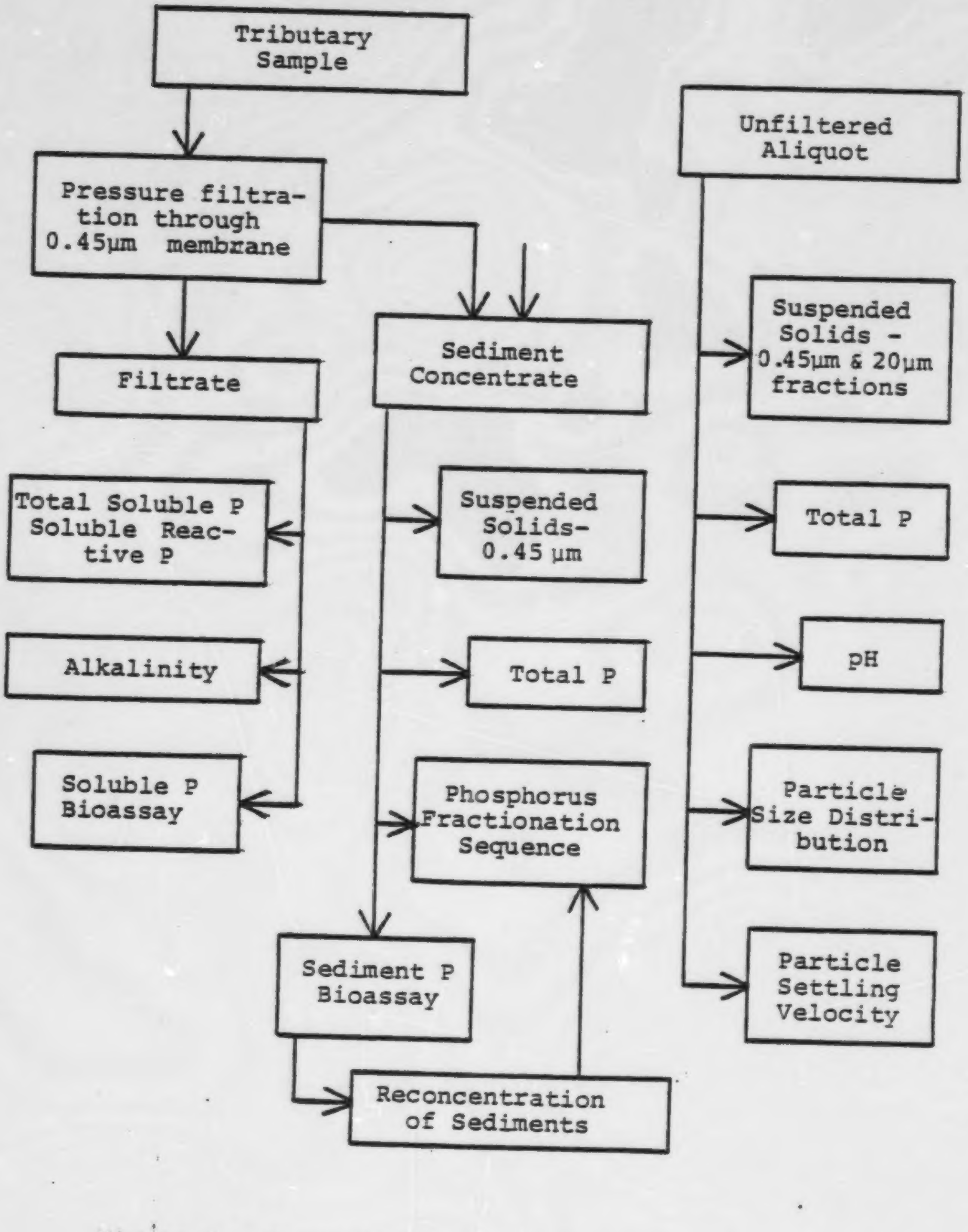

Tributary Sample
Pressure filtration through 0.45µm membrane
Filtrate
Sediment Concentrate
Unfiltered Aliquot
Total Soluble P Soluble Reactive P
Alkalinity
Soluble P Bioassay
Suspended Solids-0.45 µm
Total P
Phosphorus Fractionation Sequence
Sediment P Bioassay
Reconcentration of Sediments
Suspended Solids - 0.45µm & 20µm fractions
Total P
pH
Particle Size Distribution
Particle Settling Velocity

Figure 3. General flow chart for analysis of tributary samples.

TABLE 3. ANALYTICAL METHODS AND REFERENCES

Analysis	Method and Reference
A) Physical:	
1) Suspended Solids	Gravimetric; Drying at 103°C(APHA, *et al.*, 1976)*
2) Particle Size Distribution	Coulter Counter (Bonner, *et al.*, 1983)
3) Particle Settling Velocity	Spectrophotometric (Kwolek, 1982)
B) Chemical:	
1) Reactive Phosphorus	Ascorbic Acid Method (Murphy and Riley, 1962)
Preliminary Digestion	Persulfate (APHA, *et al.*, 1976)
2) Alkalinity	Acidimetric Titration(APHA, *et al.*, 1976)
3) pH	Glass Electrode
4) Sediment Phosphorus Fractionation	NaOH-CDB-HCl (Logan, 1978)
C) Biological:	
1) Sediment P Bioassay	Dual Culture Diffusion Apparatus (DePinto, 1982)
2) Soluble P Bioassay	Batch Incubation with *Selenastrum* (Young, *et al.*, 1982)

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*APHA, *et al.* (1976) is referred to as *Standard Methods* in the text.

Detroit River samples, only analyses appropriate to sediment concentrates were applied (i.e. center branch of Figure 3). Total P, suspended solids and P fractionation were measured on all of these samples, while bioassays were conducted on Lake Erie bluff and bottom sediment samples only.

Basic Analytical Methods

Suspended Solids--

Total suspended solids (SS) was measured by a procedure similar to that described in Standard Methods, Section 208D. A known volume of sample was filtered through a preweighed 0.45 µm pore size Nuclepore nitrocellulose membrane (47 mm diameter).

After drying at 103 °C, the weight of sediment retained on the membrane was determined by weighing on a Mettler Model A30 top-loading electronic balance. The concentration of suspended solids >20 µm was measured in the same manner, except that the 0.45 µm membrane was replaced by a 47 mm diameter disc cut from a sheet of Nitex nylon screening fabric with a pore size of 20 µm (from Tetko, Inc., Elmsford, NY).

pH and Alkalinity--

Alkalinity and pH measurements were made using an Orion Research Model 901 "microprocessor ionalyzer" with a glass combination pH electrode. Sections 402 and 403 of Standard Methods were used as guidelines for the alkalinity analysis. A 50 ml aliquot of filtered river water was titrated with a standardized acid (0.0099 N H_2SO_4) solution to below pH

4. The endpoint of the titration was taken to be the inflection point in the curve of pH versus volume of acid added, which generally occurred at a pH of 4.8-5.0.

Reactive Phosphorus--

All reactive phosphorus concentrations were determined colorimetrically using the ascorbic acid method proposed by Murphy and Riley (1962) and modified slightly in Standard Methods, Section 425F. Following addition of the mixed reagent to samples, at least 10 min. was allowed for color development. The sample was placed in a glass cell with a 10 cm path length and absorbance was measured at 880 nm using a Bausch and Lomb Spectronic 710 spectrophotometer. A set of standard solutions ranging from 0 to 200 µgP/l were prepared and analyzed along with each group of samples to provide a standard curve of reactive P concentration versus absorbance. Deionized water was used as the medium for all standards except those serving to calibrate the analysis of CDB extraction solutions. The procedures used to prepare CDB standards are discussed later in this section.

Preliminary digestion for total P analysis--

Samples analyzed for total phosphorus were subjected to a persulfate digestion (Standard Methods, Section 425C.) prior to analysis for reactive P. Separate standard curves were developed for the calculation of total P concentrations by digesting a set of standards along with the samples.

Particle Size Distribution

Procedures--

The distributions of sediment particle sizes in the unfiltered aliquots of river water were determined using a Model ZBI Coulter Counter in series with a 100 channel pulse height amplifier, or "Channelyzer" (both from Coulter Electronics, Inc., Hialeah, Florida). The Channelyzer was interfaced to a Horizon North Star microprocessor, which was used to transform calibration and channel count information into real particle number and volume distributions. Many of the procedures used for particle sizing in this study were first reported by Rodgers (1979) and have been automated by Bonner, et al. (1983).

The sizing of particles with the Coulter Counter is based on changes in resistance caused by the presence of particles in the path of an electrical current passing through an electrolyte. A flow of current is maintained between two electrodes, one immersed in the sample and the other located in the aperture tube into which the sample is drawn. As the sample containing the particles passes through the aperture (a small opening at the base of the tube), voltage pulses that are proportional to the volumes of individual particles are registered by the Channelyzer.

In order to develop correlations between Coulter Counter control settings and actual particle volumes, the instrument was calibrated using counts performed on monodisperse suspensions of polystyrene latex particles of known sizes. Calibration involves the determination of a "threshold factor" that is required to calculate the particle volume corresponding to each channel. By performing counts with both 30 μm and 50 μm apertures, it was possible to obtain accurate results for particles in an effective diameter range of 0.82-15.8 μm. At least three particle ranges were used with each aperture to optimize the resolution of the counts.

The instrument settings used for the various size ranges examined in this study are summarized in Table 4. The volume of individual particles associated with a particular channel is given by the equation (Coulter Electronics, 1979):

$$V = ((CN \times WW/100) + BCT) \times TF \qquad (5)$$

where V = volume of individual particles in a certain channel;
CN = the channel number (from 0 to 99);
WW = the window width setting;

TABLE 4. COULTER COUNTER AND CHANNELYZER SETTINGS

Range#	$\frac{1}{\text{Amplification}}$	$\frac{1}{\text{Aperture Current}}$	Lower Threshold	Upper Threshold	Threshold Factor	Base Channel Threshold	Window Width	Diameter Range (μm)
30 um aperture								
1	1/4	1/2	31.5	79	.009425	30	50	0.8188 - 1.1245
2	1	1/2	20.8	97.9	.0377	19	80	1.1255 - 1.914
3	2	1	25.3	101.9	.1508	23.5	80	1.913 - 3.085
50 um aperture								
1	2	1/2	7	104	.3025	5	100	1.513 - 3.904
2	2	2	26	105	1.21	25	82	3.908 - 6.244
3	8	2	26	105	4.84	25	82	6.203 - 9.912
4	32	2	26	105	19.36	25	82	9.93 - 15.768

BCT = the base channel threshold setting;
and TF = the threshold factor determined by calibration with standardized particles.

In this study, the effective particle diameter corresponding to each channel was calculated from this volume by assuming a spherical particle geometry.

The electrolyte in which the particles were suspended for analysis was a 0.6% sodium chloride solution. A thickening agent, polyvinylpyrollidone, was added to slow the passage of particles through the aperture, thus providing greater accuracy in the measurement of particle volumes. The composition of the electrolyte solution and the preparation procedure are given in Table 5. Samples were prepared for counting by diluting aliquots of unfiltered river water with the electrolyte solution.

Inaccuracies may result in counting samples with high particle concentrations due to the simultaneous passage of two or more particles through the aperture. In addition, excessive dilution of samples may result in a particle size distribution that is not representative of the original sample. In this study, dilutions were chosen to provide as high a particle concentration as possible, without exceeding a maximum cumulative count of 200,000 particles/ml in each diameter range. Counts were performed on 0.1 ml aliquots of the appropriate sample dilution. Depending on the reproducibility of cumulative particle counts, between two and five replicate measurements were made in each diameter range. These were averaged and used to calculate the frequency distribution of sediment particle sizes.

Data Analysis--

The particle size distribution data for each tributary sample was analyzed using both a power law distribution function and a plot of cumulative particle volume versus particle diameter. The size distribution of aquatic suspensions can often be described by a mathematical relationship of the form (Lerman, et al., 1977; Lawler, 1979):

$$dN/d(d_p) = A\ d_p^{-\beta} \qquad (6)$$

where $d(d_p)$ = the particle diameter range being examined;
dN = the number of particles falling within that diameter range;
A = a coefficient related to the total concentration of particulate matter;
and β = the power law exponent.

TABLE 5. ELECTROLYTE SOLUTION - 0.6% ISOTONE (FROM AUTENRIETH, 1981)

Compound	g/l
NaCl	6.0
Sodium azide	1.0
Polyvinylpyrrolidone-PVP-40T*	35.0
$Na_2HPO_4 \cdot 12H_2O$	0.32
$NaH_2PO_4 \cdot H_2O$	0.04
NaOH	0.04

*Technical grade from Sigma Chemical Co., St. Louis, Missouri.

Procedures -

1) Add the first three ingredients to 1 liter of deionized water. Stir magnetically on very low heat until all three ingredients have been added.

2) Very slowly add the polyvinylpyrrolidone. It should take 45 to 60 minutes to add this compound (for a 1 liter batch).

3) When the polyvinylpyrrolidone has dissolved, add the remaining ingredients. Stir until completely dissolved.

4) Filter solution through a 0.2 µm filter and store in an acid-washed container.

The power law exponent, β , is equal to the negative slope of a log-log plot of $dN/d(d_p)$ versus d_p. In this study, such plots were used to obtain two values of β for each tributary sample, one based on particle counts made with the 30 µm aperture and the other on counts with the 50 µm aperture. The theoretical development of the power law function and the significance of the value of β are discussed in greater detail in Appendix A.

The Coulter Counter data was also used to generate plots of cumulative particle volume versus particle diameter. From these plots, the contribution of each diameter range to the total volume of particles could be examined. Also, the plots were used to evaluate the volume-weighted median particle diameter, i.e. the diameter below (and above) which 50% of the total particle volume is contained.

Chemical Fractionation of Sediment Phosphorus

The sediment phosphorus fractionation scheme employed in this study was based on a procedure originally outlined by Williams, *et al*. (1971b) involving sequential extractions with NaOH, CDB, and HCl reagents. This sequence has been used more extensively and described in detail by Logan (1978). A summary of the procedure is shown in Figure 4. First, the volume of sediment concentrate equivalent to 100 mg (dry weight) of sediments was pipetted into a centrifuge tube and centrifuged at 900 x g for 20 min. in an International Equipment Co. Model UV centrifuge with a swinging bucket rotor. The extractions were then carried out as indicated in Figure 4. After both the NaOH and CDB extraction steps, the sediments were resuspended and rinsed with the same P-free media used to prepare the sediment concentrates (see footnote in Table 6).

During the second year of the project, the quantity of sediments and volumes of extractants used were modified to accomodate the use of a Beckman Model J2-21 centrifuge with a fixed angle rotor. The following changes were made in the procedure:

1) Dry weight of sediments - 60 mg
2) Volumes of extraction reagents:
    a) 0.1 N NaOH - 37 ml
    b) 1.1 M $NaHCO_3$ - 4 ml
    c) 0.25 M Na-citrate - 33 ml
    d) 1.0 N HCl - 37 ml
3) Centrifugation - 31,000 x g for 30 min.

The extract solution from each step of the fractionation was decanted into an erlenmeyer flask (following centrifugation) for storage prior to analysis. Aliquots of the NaOH and HCl extracts were neutralized to just below the phenolphthalein endpoint

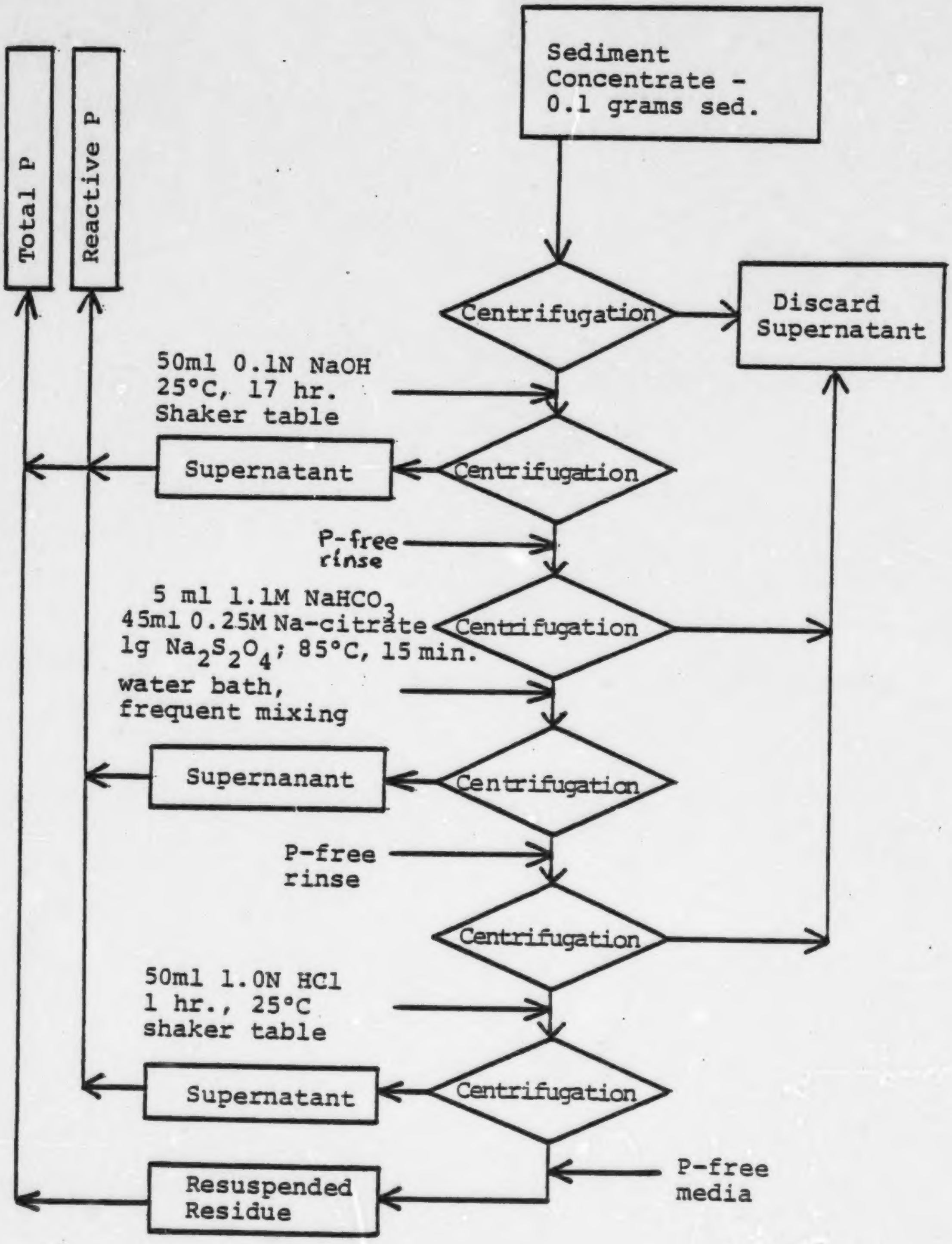

Sediment Concentrate - 0.1 grams sed.
Total P
Reactive P
Centrifugation
Discard Supernatant
50ml 0.1N NaOH
25°C, 17 hr.
Shaker table
Supernatant
Centrifugation
P-free rinse
5 ml 1.1M NaHCO3
45ml 0.25M Na-citrate
1g Na2S2O4; 85°C, 15 min.
water bath,
frequent mixing
Centrifugation
Supernanant
Centrifugation
P-free rinse
Centrifugation
50ml 1.0N HCl
1 hr., 25°C
shaker table
Supernatant
Centrifugation
P-free media
Resuspended Residue

Figure 4. Procedure for chemical fractionation of sediment P.

(pH 8.3) with 6 N H_2SO_4 and/or 2 N NaOH, and diluted by an appropriate factor, before analysis of reactive phosphorus to determine the R-NaOH-P and HCl-P fractions. Total phosphorus analyses were performed on the NaOH extracts and the resuspended sediment residue remaining at the end of the fractionation sequence (T-NaOH-P and Residual-P fractions). Suitable volumes of each were pipetted into erlenmeyer flasks, brought up to about 50 ml with deionized water, and digested via the persulfate method. No adjustment in pH was made prior to the addition of the digestion acid to these samples.

Before measuring the reactive P concentrations of CDB extracts, it was first necessary to eliminate interferences caused by both sodium citrate and sodium dithionite. This was accomplished by following the procedures suggested by Weaver (1974). Excess dithionite was oxidized by bubbling moist air through the CDB extract solutions for at least four hours. The extracts were then brought up to a volume of 50 ml with deionized water, and a 5 ml aliquot was removed for the reactive P analysis. The citrate interference was eliminated by the addition of 4.3 ml of 4% ammonium molybdate to the 5 ml of CDB extract. This mixture was diluted to a final volume of 50 ml in a volumetric flask and analyzed for reactive P by the ascorbic acid method. Blank and standard solutions used to develop standard curves for the analysis of CDB-P were prepared in a medium containing 1 g of sodium dithionite and 25 ml of 0.25 M sodium citrate per 50 ml of final solution volume. Interferences were eliminated from the standards by bubbling and by the addition of 3.75 ml of 4% ammonium molybdate to 5 ml aliquots of solution before dilution to a 50 ml final volume.

Sediment Particle Settling Velocities

Measurements of median particle settling velocities were made for 28 unfiltered tributary samples using a spectrophotometric technique. Absorbance readings were used as an indicator of suspended solids concentration at a fixed height in the sample cell. Measurements were made at a wavelength of 750 nm on a Perkin-Elmer 559-A UV/VIS spectrophotometer. Median particle settling velocities were calculated based on the time required for decays in absorbance to 20% and 50% of the initial reading and the distance from the top of the sample cell to the center of the light path. A detailed description of this procedure and its applicability was presented by Kwolek (1982). The accuracy of the results appear to be adversely affected by changes in the absorbance characteristics of sediments as a function of particle size and by vibrations in the instrument. Kwolek (1982) found that the measured settling velocities for spherical glass particles with volume-weighted median particle diameters of 3.78 μm and 7.60 μm were 43% and 23% less, respectively, than the velocities predicted by Stoke's Law. However, the procedure may be useful in identifying changes in the settling behavior of suspended river sediments during the course of storm runoff events.

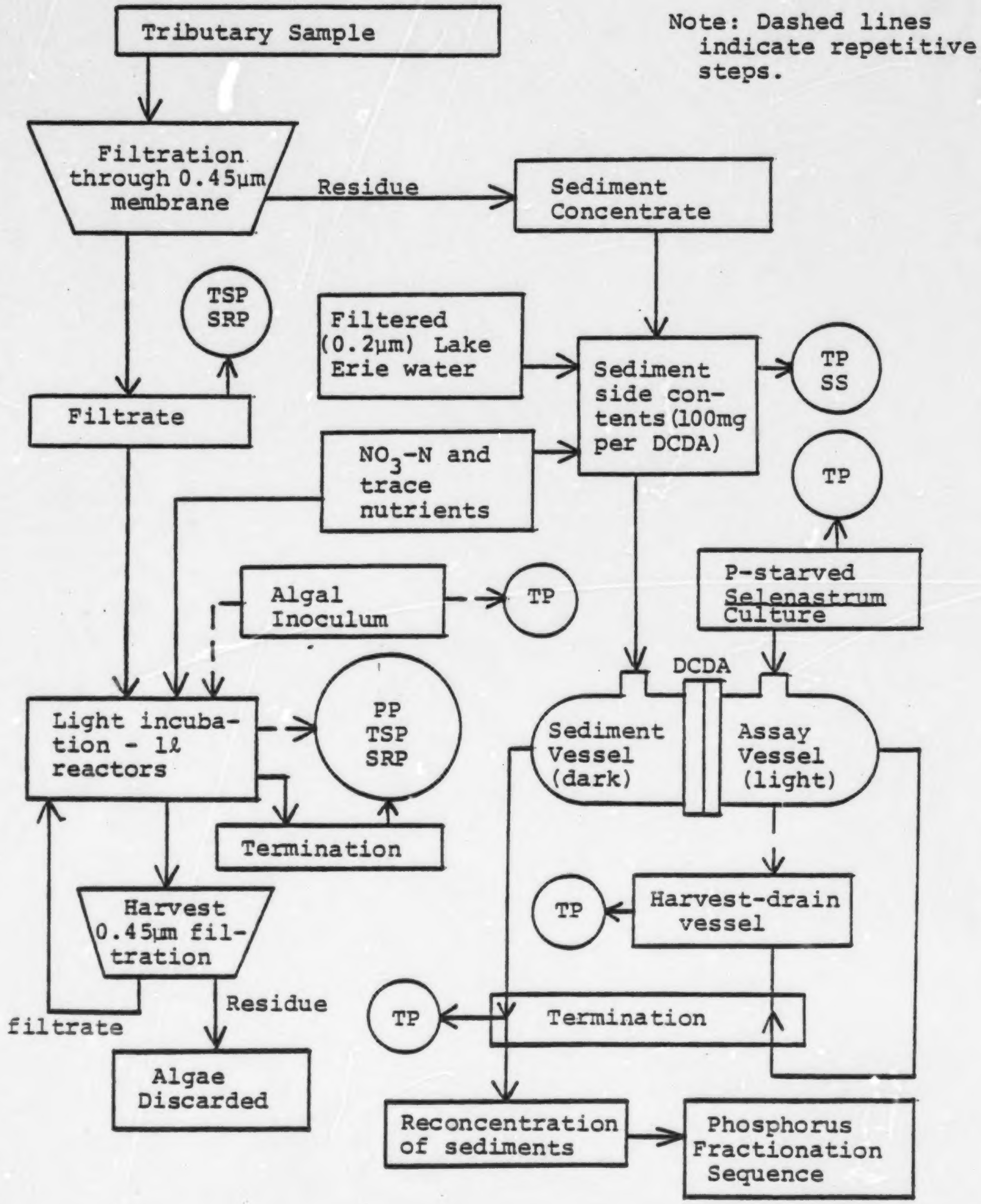
Sediment Phosphorus Bioassays

Procedures--

The bioavailability of sediment-bound phosphorus was measured using the bioassay technique proposed by DePinto (1982). A summary of the procedure is shown on the right-hand side of Figure 5. The Dual Culture Diffusion Apparatus (DCDA) reactor vessels were manufactured from 70 mm O.D., standard wall Pyrex tubing. Half of these were painted black in order to suppress photosynthetic activity by algae indigenous to the tributaries that may have been present in the sediment vessels. The sediment and assay vessels were separated by a 90 mm diameter Nuclepore polycarbonate membrane with a 0.4 µm pore size and were held together by a hinged clamp made from two modified 57 mm McCarter clamps. Rubber gaskets with a light coating of silicone stopcock grease were used to provide a water-tight seal between the glass flanges of the reactor vessels and the membrane. A drawing of an assembled DCDA reactor is presented in Figure 6, and a photograph is shown in Figure 7.

The assay organism used in this study was P-starved *Selenastrum capricornutum*, a green alga, obtained from the University of Texas at Austin collection (UTEX 1648). Stock cultures of *Selenastrum* were grown in deionized water spiked with the necessary macro- and micro-nutrients. The concentrations of nutrients added are listed in Table 6. This mixture is a modification of the synthetic growth medium proposed by Guillard and Lorenzen (1972), and contains 200 µgP/l. These cultures were grown in 250 ml erlenmeyer flasks with cotton stoppers on a shaker table under 300 ft-ca of continuous cool-white fluorescent lighting. New stock cultures were started in autoclaved media every 7 to 14 days. Algal cultures for the bioassays were grown in Lake Erie water that was collected at the City of Buffalo water treatment plant and filtered through a 0.2 µm pore size Nuclepore nitrocellulose membrane. This water was spiked with 20 µgP/l (0.1 ml of stock solution 8 per liter) and all other nutrients at the levels indicated in Table 6. The total concentration of phosphorus in the spiked Lake Erie water was typically 25-30 µg/l.

To prepare the algal growth media for inoculation, all of the nutrients except $FeCl_3$ and the tri-vitamin solution (solutions #9 and #10 from Table 6) were first added to 8 l of filtered Lake Erie water. This was then filtered under positive pressure through an autoclaved 0.2 µm pore size Nuclepore nitrocellulose membrane and into an autoclaved 9 l glass vessel. Following addition of the iron and vitamins, the media was inoculated with 8 ml of a stock culture of *Selenastrum*. The


Tributary Sample
Filtration through 0.45µm membrane
Residue
Sediment Concentrate
TSP
SRP
Filtered (0.2µm) Lake Erie water
Sediment side contents (100mg per DCDA)
TP
SS
Filtrate
NO3-N and trace nutrients
TP
P-starved Selenastrum Culture
Algal Inoculum
TP
DCDA
Light incubation - 1ℓ reactors
PP
TSP
SRP
Sediment Vessel (dark)
Assay Vessel (light)
Termination
Harvest 0.45µm filtration
TP
Harvest-drain vessel
filtrate
Residue
TP
Termination
Algae Discarded
Reconcentration of sediments
Phosphorus Fractionation Sequence

Note: Dashed lines indicate repetitive steps.

Figure 5. Procedures for bioassay measurements of phosphorus availability.

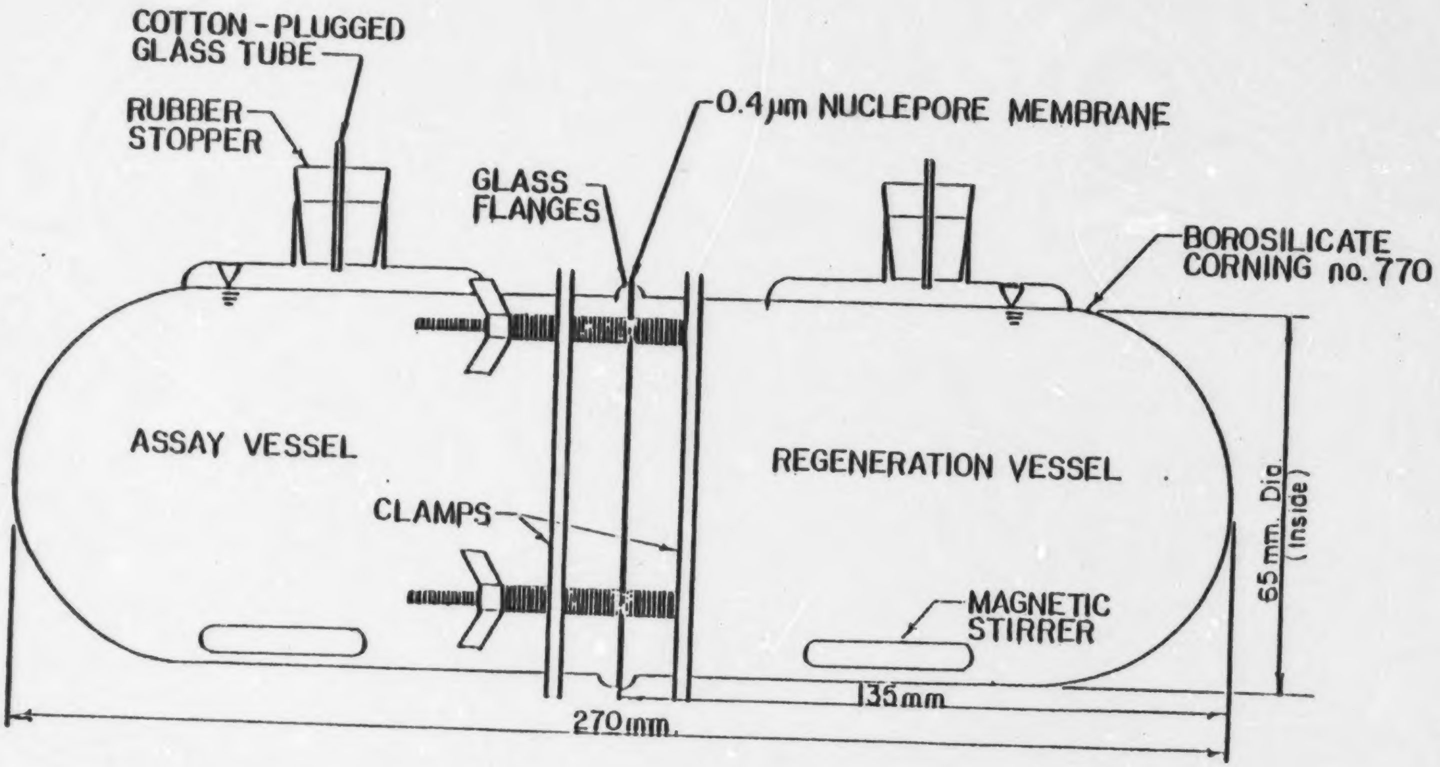

COTTON - PLUGGED GLASS TUBE
RUBBER STOPPER
GLASS FLANGES
0.4 μm NUCLEPORE MEMBRANE
BOROSILICATE CORNING no. 770
ASSAY VESSEL
REGENERATION VESSEL
CLAMPS
MAGNETIC STIRRER
65 mm. Dia. (Inside)
135 mm
270 mm.

Figure 6. Assembled DCDA reactor.

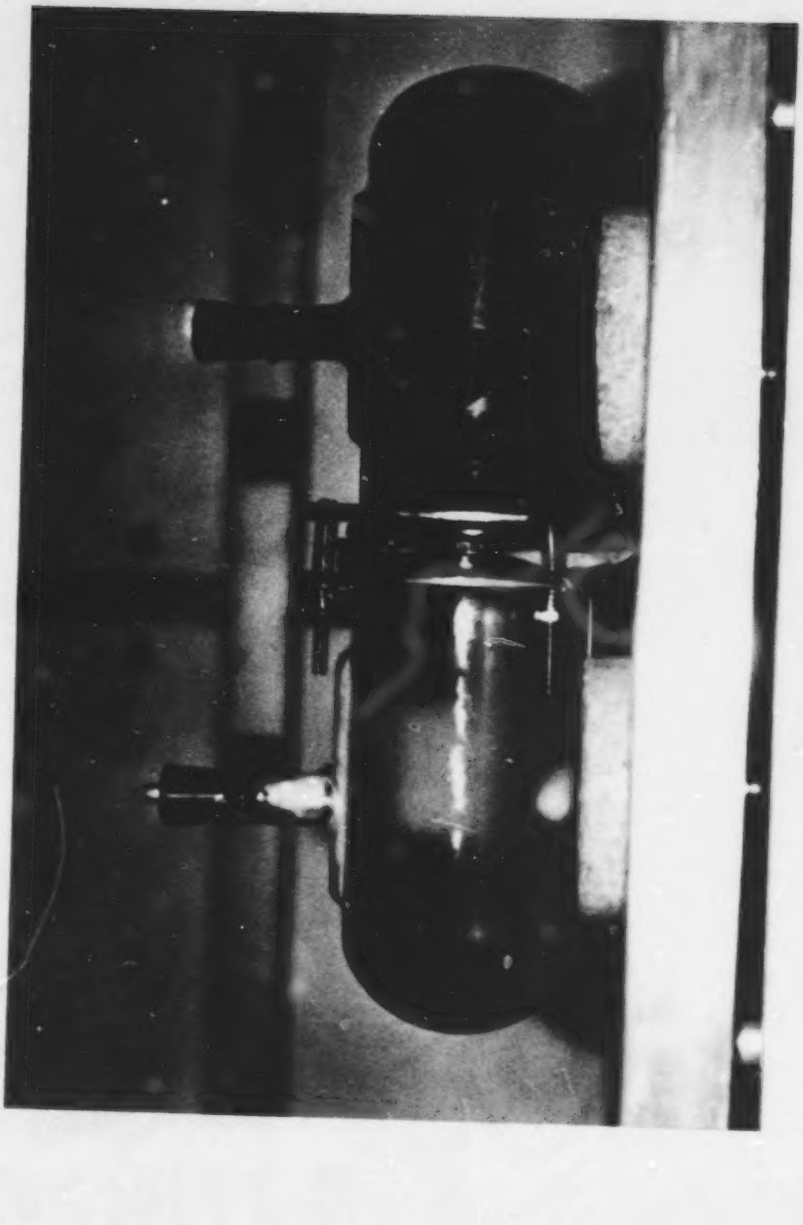


Figure 7. Photograph of Assembled DCDA Reactor.

TABLE 6. COMPOSITION OF ALGAL GROWTH MEDIA
(MODIFIED FROM GUILLARD AND LORENZEN, 1972)

Chemical Compound (M.W.)	Stock Concentration (g compound/l)	ml of stock added per l of media
1) $CaCl_2 \cdot 2H_2O$ (147.02)	36.755	1
2) $MgSO_4 \cdot 7H_2O$ (246.365)	36.970	1
3) $NaHCO_3$ (83.9998)	12.600	1
4) Na_2EDTA	4.36	2
5) Trace Metal Solution		1
$CuSO_4$ (159.54)	0.0064	
$ZnSO_4 \cdot 7H_2O$ (287.44)	0.023	
$CoCl_2 \cdot 6H_2O$ (237.84)	0.0119	
$MnSO_4 \cdot H_2O$ (168.998)	0.152	
$Na_2MoO_4 \cdot 2H_2O$ (218.930)	0.0066	
6) H_3BO_3 (64.81)	1.00	1
7) KNO_3 (101.096)	26.288	1
8) $Na_2HPO_4 \cdot 12H_2O$ (357.953)	2.328	1
9) $FeCl_3 \cdot 6H_2O$ (270.206)	3.1605	1
10) Tri-Vitamin Solution		1
Biotin	0.0005	
B_{12}	0.0005	
Thiamine	0.10	

- All stock solutions were made up in deionized water.
- The P-free media used to make up sediment concentrates and to rinse sediments during fractionations contained solutions #1, 2, and 3 only.

cultures were placed in an incubator at 20 °C with continuous cool-white fluorescent lighting (500 ft-ca) and magnetic stirring, and were utilized for bioassay experiments after a growth period of between 5 and 12 days.

The suspensions placed in the sediment vessels of the DCDAs were prepared by spiking filtered Lake Erie water with nutrient solutions #4, 5, 6, 7 and 9 from Table 6 (to ensure P-limited growth throughout the bioassays) and adding an aliquot of sediment concentrate. In most cases, these suspensions contained 100 mg of sediments per 400 ml of final volume, although larger amounts were used in analyzing Cattaraugus Creek and Lake Erie bluff sediments. Sediment suspensions were usually made up in 1.5 l batches to allow triplicate DCDA bioassays and storage of an aliquot for suspended solids and total P analyses.

Following assembly of the DCDAs, 400 ml aliquots of well-mixed sediment suspension and Selenastrum capricornutum assay culture were measured out in graduated cylinders and added to the dark and light sides, respectively, of each reactor. A rubber stopper with a cotton-filled glass tube through the center was placed in the opening of both sediment and assay vessels. The reactors were then placed on magnetic stir tables under cool-white fluorescent lighting (300 ft-ca) at 20 °C and stirred continuously with 31.8 mm (length) egg-shaped magnetic stir bars placed in both vessels.

The DCDAs were sampled periodically by first working the stir bar around the inside of the assay side to remove any attached algae from the walls of the vessel, and then decanting the entire assay side contents into an erlenmeyer flask. This was replaced by 400 ml of a fresh P-starved assay culture and the incubation was continued. The reactors were generally sampled at 3, 7, 14, and 21 days after startup of the bioassay run. Several of the reactors were also sampled at 28 days. Upon termination of the experiments, the contents of the sediment side were decanted and retained for total P analysis as well. The release of phosphorus from the sediments was monitored by measuring the differences in total P concentrations of the assay cultures before and after incubations in the DCDAs. This approach is contingent upon the rapid diffusion of soluble phosphorus across the membrane to the assay side for algal uptake. In a preliminary experiment, diffusion was found to occur at an average first-order rate of 2.065 day^{-1} (base e). A detailed description of this experiment and the results obtained are presented in Appendix B.

Data Analysis--

Experimental observations have indicated that the uptake of phosphorus by the assay algae in DCDA bioassays can be described mathematically by a first-order saturation function having the following form:

$$Q_2(t) = P_{ult}\ [1 - \exp(-k_r t)] \tag{7}$$

where $Q_2(t)$ = the total amount of P taken up by the algae in the assay vessel (vessel #2) at time t (μgP/g sediment);

P_{ult} = the total amount of sediment P ultimately available for algal uptake (μgP/g sediment);

and k_r = the first-order P release rate (day^{-1}), base e.

DePinto (1982) has derived a similar expression by writing mass balance equations for phosphorus in the two DCDA vessels and making appropriate assumptions. The derivation of Equation 7 is presented in Appendix C. This mathematical development also shows that, under certain conditions, the expression for algal uptake of P on the assay side is identical to that for the release of P from the sediments.

The bioassay experiments provided phosphorus release data in the form of $Q_2(t)$ for various values of t. From this data, values of P_{ult} and k_r were calculated using the Thomas Method, which is based on the similarity of two series functions. This method involves the determination of the slope (b) and intercept (a) of a linear regression of $(t/Q_2(t))^{1/3}$ versus $Q_2(t)$. P_{ult} and k_r are then calculated using the equations (Thomas, 1950):

$$k_r = 6b/a \tag{8}$$

$$P_{ult} = 1/k_r a \tag{9}$$

Soluble Phosphorus Bioassays

During the first year of this study, an additional 2 l of filtered river water was collected during pressure filtration of 14 of the tributary samples to allow bioassay analysis of the availability of soluble (filterable) P. The bioassay technique used was similar to that described by Young, *et al*. (1982). A summary of the procedure is shown on the left-hand side of Figure 5. Two 1 liter aliquots of filtered river water were placed in 1 liter glass bottles and spiked with nutrients #4, 5, 6, 7 and 9 to ensure P-limited algal growth. These bottles, or "batch reactors", were inoculated with 3 or 4 ml of a concentrated suspension of *Selenastrum capricornutum*, and placed on a shaker table at 20 °C under fluorescent lighting. Concentrated inocula were obtained by centrifuging P-starved assay cultures (described earlier), discarding the supernatant and resuspending the algae in about 20 ml of P-free media per liter of initial culture volume. An aliquot of each inoculum was saved and analyzed to determine the amount of particulate P added to the batch reactors. The initial TSP and SRP concentrations of the filtered river water were measured as a part of the routine analyses performed on all tributary samples.

After 1 day of incubation, 100 ml of the batch reactor contents was removed and analyzed for particulate, total soluble, and soluble reactive P fractions. Subsequent samplings were conducted at 3 to 5 day intervals thereafter, and involved the withdrawal of 50 ml for particulate P and total soluble P analyses. In some cases, one of the samplings was accompanied by removal of the algae via filtration through a 0.45 µm Nuclepore nitrocellulose membrane and addition of a fresh P-starved inoculum to the reactors.

SECTION 6

RESULTS AND DISCUSSION

ROUTINE ANALYSES ON UNFILTERED TRIBUTARY SAMPLES

The results of TP, TSP, and SRP analyses and suspended solids (>0.45 µm and >20 µm) measurements performed on unfiltered aliquots of the tributary samples are summarized in Table 7. Mean values of tributary discharge, pH, and filtrate alkalinity are also presented. A listing of all individual measurements of these parameters is given in Appendix D. For all of the tributaries except the Genesee, the samples collected represent a wide range of flow conditions. However, all samples were collected during storm runoff events, so low (or baseline) flows were not included. Total suspended solids (SS) concentrations increased markedly with increases in flow for all of the tributaries. As a result, total P concentrations generally showed greater variability than soluble P levels. The mean concentrations of soluble P in the Ohio tributaries were considerably higher than in the New York tributaries. Therefore, suspended sediments would be more likely to accumulate P by adsorption during transport in the Ohio rivers.

SEDIMENT P FRACTIONATION RESULTS

Total Sediment P (T-Sed-P) Measurements

The data obtained from the chemical extraction of tributary suspended sediments are summarized in Table 8. A listing of results obtained for the individual samples is presented in Appendix D. The mean extractable fractions for each tributary are expressed both in µg of P extracted per gram of sediment and as a percentage of total sediment P (T-Sed-P). Two separate measurements of the total P content of sediments are given in Table 8. The first of these is based on TP and suspended solids analyses performed on sediment concentrates (T-Sed-P = TP/SS), while the second is calculated from the TP, TSP, and SS concentrations of raw river water samples (i.e. (TP-TSP)/SS). Unless otherwise indicated, the former values are used as the basis for the following discussion, as well as for all calculations.

T-Sed-P concentrations showed little variation among samples from a given tributary. The coefficients of variation ranged from 6.2% for the Cuyahoga River to 16.5% for Honey Creek.

TABLE 7. SUMMARY OF PHYSICAL AND CHEMICAL MEASUREMENTS ON UNFILTERED TRIBUTARY SAMPLES AND FILTRATES

Tributary	Flow* (m^3/s)	pH	Filtrate Alkalinity (mg/ℓ as $CaCO_3$)	Suspended Solids (mg/ℓ)		Phosphorus Concs. (µg/ℓ)		
				Total†	% < 20 µm	TP	TSP	SRP
Maumee River:								
Mean	647.0(11)††	7.88(7)	119.5(5)	310.5(11)	86.1(6)	501.2(11)	111.8(11)	97.4(11)
C.V. (%)**	75.3	3.6	26.6	78.6	23.7	58.9	15.5	15.1
Sandusky River:								
Mean	222.7(27)	7.84(7)	90.0(7)	701.8(27)	85.0(11)	851.6(27)	81.0(27)	66.9(27)
C.V. (%)	83.1	3.8	48.9	124.7	13.6	103.0	28.3	31.0
Cuyahoga River:								
Mean	108.6(5)	7.56(4)	65.3(3)	256.2(5)	62.3(4)	412.2(5)	77.9(5)	63.3(5)
C.V. (%)	50.6	1.9	4.0	82.3	13.0	44.2	61.3	84.4
Cattaraugus Creek:								
Mean	29.5(5)	7.80(5)	67.8(5)	1707.3(3)	62.8(3)	1090.7(3)	13.9(5)	6.3(5)
C.V. (%)	75.3	4.5	35.1	133.6	21.8	138.2	19.2	49.2
Honey Creek:								
Mean	51.5(4)	-	-	892.2(4)	91.8(2)	1071.6(4)	96.3(4)	79.8(4)
C.V. (%)	84.5			96.6	4.2	69.3	52.6	58.2
Genesee River:								
n = 1	-	7.35	80.2	156.0	88.5	192.0	37.0	18.3

* Values given are instantaneous flows at time of sample collection, except those for the Cuyahoga River, which are average daily flows.

† Amount retained on a membrane filter with a pore size of 0.45 µm.

** Coefficient of variation (C.V.) = (Standard Deviation/Mean) x 100%.

†† Values in parentheses are the number of measurements made.

TABLE 8. SUMMARY OF P FRACTIONATION RESULTS FOR TRIBUTARY SUSPENDED SEDIMENTS

Triburary	T-SED-P	(TP-TSP) SS	Concentrations in μgP/g sediment T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCℓ-P	Residual P
Maumee River (n=9):								
Mean	1,259	1,244	403(32.0)*	273(21.7)	131(10.4)	238(18.9)	117(9.3)	174(13.8)
C.V. (%)	14.3	18.9	32.4	20.9	61.9	17.5	32.5	42.2
Sandusky River (n=25):								
Mean	1,188	1,193	449(37.7)	298(25.1)	151(12.7)	237(20.0)	77(6.5)	194(16.3)
C.V. (%)	11.7	13.6	20.8	20.8	31.1	21.0	35.6	42.5
Cuyahoga River (n=4):								
Mean	1,315	1,246	575(43.8)	442(33.6)	133(10.1)	280(21.3)	188(14.3)	73(5.6)
C.V. (%)	6.2	9.9	13.4	21.4	29.6	16.6	6.3	63.9
Cattaraugus Creek (n=5):								
Mean	637	588	76(11.9)	46(7.2)	30(4.7)	82(12.9)	305(47.9)	48(7.5)
C.V. (%)	11.0	12.0	33.2	27.2	46.5	22.7	12.9	8.7
Honey Creek (n=4):								
Mean	1,189	1,218	505(42.5)	356(30.0)	149(12.5)	203(17.1)	56(4.7)	265(22.3)
C.V. (%)	16.5	14.5	19.1	23.5	11.3	22.2	50.7	21.7
Genesee River (n=1):								
	957	994	240(25.1)	170(17.8)	69(7.2)	187(19.5)	273(28.5)	77(8.0)
Detroit River (n=1)†:								
	1,424	-	596(41.9)	305(21.4)	291(20.4)	177(12.4)	323(22.7)	170(11.9)

* Values in parentheses are means expressed as a percentage of T-Sed-P.

† Sediments composited from four sampling locations.

Samples were collected from three of the tributaries (Maumee, Sandusky, and Cuyahoga) during both 1980 and 1981. The mean T-Sed-P concentrations for 1981 samples slightly exceeded the 1980 values for all rivers where a comparison was possible. However, greater differences in sediment P concentrations were observed between tributaries. The coefficient of variation (C.V.) calculated from the mean T-Sed-P levels for all tributaries was 23.1%.

Suspended sediments from Cattaraugus Creek contained markedly lower levels of P than those from any of the other rivers. The T-Sed-P concentration measured for the only Genesee River sample collected was well above the mean for Cattaraugus Creek, but still considerably less than the Ohio tributary averages. Differences in the total sediment P levels among the Ohio rivers were relatively small. Cuyahoga River sediments did contain slightly more P than the others, possibly due to a greater degree of influence from urban sources. Point source inputs of P were probably also responsible for the fairly high levels of T-Sed-P found in the Detroit River composite sample.

In comparing the findings of this study and previous ones, consideration should be given to the techniques used to determine total sediment P concentrations and discrepancies that may exist between the various methods. A summary of data obtained by other researchers on the rivers sampled in this study is presented in Table 9 for comparison to the results in Table 8. Logan (1978) found considerable disagreement among different measurements of total sediment P. Perchloric acid digestions on freeze-dried sediments gave T-Sed-P results somewhat higher than persulfate digestions on freeze-dried sediments, but still well below the values calculated from the TP, TSP, and SS concentrations of raw river water. In the present study, total sediment P concentrations obtained by the latter method agreed reasonably well with those derived from persulfate digestion of sediment concentrates. T-Sed-P concentrations reported by Logan (1978), Baker (1982a), and Armstrong *et al*. (1979) were mostly greater than those obtained in this study, while those reported by Baker (1982b) and Reddy (1980) were somewhat lower.

Flux-weighted mean T-Sed-P concentrations computed by Baker (1982a) indicate that the phosphorus content of sediments transported by a particular river may vary considerably from year to year. As was mentioned previously, only small fluctuations were seen between 1980 and 1981 samples in the present study. In addition, T-Sed-P levels appeared to remain relatively constant over a wide range of flow conditions and suspended solids concentrations for any given tributary. Based on a large number of samples from Honey Creek, however, Baker (1982a) demonstrated an inverse relationship between T-Sed-P (i.e., PP/SS) and SS concentrations.

TABLE 9. RESULTS OF CHEMICAL ANALYSES ON TRIBUTARY SEDIMENTS FROM PREVIOUS STUDIES

A) Logan (1978) - All values are expressed in μgP/g sed. Values in parentheses are extractable fractions as a percent of perchloric T-Sed-P.

River/Site	n	T-Sed-P* (PP/SS)	Persulfate† T-Sed-P	Perchloric† T-Sed-P	R-NaOH-P	CDB-P	HCl-P	Residual P
Maumee River								
Waterville	3	1792	1142	1234	334(27.1)	423(34.3)	157(12.7)	91(7.4)
All Sites	5	1648	1079	1235	315(25.5)	380(30.8)	147(11.9)	107(8.7)
Sandusky River								
Fremont	3	1448	1092	1265	389(30.8)	302(23.9)	109(8.6)	113(8.9)
All Sites	7	1865	1011	1195	362(30.3)	299(25.0)	140(11.7)	95(7.9)
Cattaraugus Creek								
South Branch	1	1129	614	724	76(10.5)	131(18.1)	271(37.4)	69(9.5)
All Sites	3	737	640	693	61(8.8)	133(19.2)	326(47.0)	73(10.5)
Honey Creek								
Melmore	4	1555	915	1195	400(33.5)	286(23.9)	52(4.4)	80(6.7)
Cuyahoga River								
Independence	1	7404	-	-	1332	1446	179	108

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* TP and TSP measured on raw river water using perchloric acid digestion.

† Based on analysis of freeze-dried sediment.

(continued)

TABLE 9 (continued)

B) Baker (1982b) - R-NaOH-P is given as a percent of the total sediment P value in the previous column.

River Site	n	T-Sed-P* (PP/SS)	R-NaOH-P (%)
Sandusky/Fremont	64	1,077 µg/g	23.0%
Honey Creek/Melmore	61	1,040	22.7

* TP and TSP measured on raw river water using persulfate digestion.

C) Baker (1982a) - Flux-weighted mean sediment P concentrations.

River Site	1975	1976	1977	1978	1979
Maumee/Waterville	1660	1420	1590	2060	-
Honey Creek/Melmore	-	1990	2210	2520	1630
Sandusky/Fremont	1520	1660	1940	1910	1570

* Based on TP and SRP analyses (i.e., PP=TP-SRP). TP digestion was performed by persulfate method.

D) Armstrong *et al*. (1979) - Mean values (in µgP/g sediment) for >0.2 µm suspended sediment fraction.

River Site	n	T-Sed-P (PP/SS)*	R-NaOH-P†	HCℓ-P**
Genesee††	15	833	162(19.4)	284(34.1)
Maumee/Waterville	4	1398	469(33.5)	273(19.5)

Values in parentheses are R-NaOH-P as a percent of T-Sed-P.

* Based on TP, SRP and SS analyses on river water, using 0.2 µm as the cutoff between dissolved and particulate material.

† Performed at 2000:1 solution:sediment ratio rather than the 500:1 used in this study and by Logan (1978).

** Performed immediately after the NaOH extraction.

†† All samples were taken upstream of Rochester, NY.

Comparison of Chemical Fractions

Comparing the means of the extractable fractions in Table 8, T-NaOH-P was found to be the largest fraction for all of the Ohio tributaries sampled, ranging from 32.0% of T-Sed-P for the Maumee River to 43.8% for the Cuyahoga River samples. In the Ohio rivers, the CDB-P fraction consistently accounted for about 20% of T-Sed-P, while HCl-P was the smallest fraction for all of those tributaries except the Cuyahoga. On the other hand, HCl-P was the largest fraction for all of the samples obtained from New York rivers. The T-NaOH-P and CDB-P fractions for the Genesee River sample were only slightly less than HCl-P, while Cattaraugus Creek sediments were found to contain roughly four times as much HCl-P as either T-NaOH-P or CDB-P. The concentrations (in μgP/g sed) of both T-NaOH-P and HCl-P in the Detroit River composite sediments exceeded the mean levels for all other tributaries. The magnitude of the Residual P fraction showed considerable variability among the tributaries sampled, ranging from the smallest of all fractions measured for the Cuyahoga River to the second largest for Honey Creek.

Concentrations of most of the extractable fractions were consistent among the samples for a given tributary. Residual-P exhibited substantial fluctuations for samples from the Maumee, Sandusky and Cuyahoga Rivers, while for the Cattaraugus Creek and Honey Creek samples, this fraction was relatively constant. Variations in the other fractions were generally limited to one or two unusually high or low values. Increases in all fractions were observed from 1980 to 1981 for samples from the Maumee and Sandusky Rivers. This is most likely due to a reduction in sediment loss during the extraction sequence, achieved through the use of a high-speed centrifuge (Beckwith, 1982). Good agreement was obtained between the two years for Cuyahoga River samples. Again, as with total sediment P concentrations, greater variability in the extractable P forms was seen between tributaries than among samples from any one tributary. The coefficients of variation for the individual fractions, calculated from the means for all tributaries, were:

T-NaOH-P - 46.4%
R-NaOH-P - 47.6%
NR-NaOH-P - 60.0%
CDB-P - 31.4%
HCl-P - 58.0%
Residual P - 54.1%

Thus, it appears that temporal variations in the forms of phosphorus bound to suspended sediments in streams are of minor importance compared to differences in soil type and land use, at least for periods of high flow associated with stormwater runoff.

The chemical fractionation results in Table 8 can provide insights into the forms and mobility of phosphorus associated with suspended sediments from the different tributaries. The sum of the R-NaOH-P and CDB-P fractions may be considered to represent the concentration of non-apatite inorganic P (NAIP) in the suspended sediments, while HCl-P provides an estimate of apatite P. Thus, the Ohio tributaries contained high levels of NAIP and only small amounts of apatite P, while Cattaraugus Creek sediments were rich in apatite P and low in NAIP. The Genesee River and Detroit River samples contained intermediate levels of both NAIP and apatite P.

The R-NaOH-P component of NAIP is thought to be mostly adsorbed to Fe and Al oxides near the surface of sediment particles, while the CDB-P fraction is occluded within the crystalline matrices of similar compounds. Logan et al. (1979) used R-NaOH-P as a measure of short-term bioavailable sediment P and NAIP (R-NaOH-P + CDB-P) as a measure of the total amount potentially releaseable over a long period of time. Thus, based on the percentages of T-Sed-P present as NAIP, the ultimate bioavailability of sediment P for the seven tributaries studied would be expected to fall in the order: Cuyahoga > Honey Creek > Sandusky > Maumee > Genesee > Detroit > Cattaraugus. It is interesting to note that the mean ratio of (R-NaOH-P)/(CDB-P) for these rivers generally tended to increase as the mean NAIP concentration increased (as shown in Table 10). R-NaOH-P exceeded CDB-P for all of the Ohio rivers, while the reverse was true for the New York rivers. A likely explanation for this observation is that the sediments with the greatest capacity for accumulating P from anthropogenic sources are those that can sorb P rapidly at the particle surface, possibly due to the presence of high surface area adsorbents such as ferric oxide gel complexes. Sediments that fix P predominantly by the slower process of incorporation into the matrix of the soil particle (i.e. as CDB-P) exhibit a lower overall tendency to accumulate P. The relative importance of these mechanisms is strongly influenced by the geologic origin of the suspended sediments. In addition, the trends seen in Table 10 are no doubt accentuated by the fact that the Ohio tributary sediments are generally exposed to higher levels of soluble P and greater applications of P as a fertilizer.

The majority of the organic P associated with suspended sediments should be released as non-reactive P during NaOH extractions (NR-NaOH-P). This is calculated as the difference between T-NaOH-P and R-NaOH-P and was highest in the Detroit River sediments. Since the Detroit River water originates almost exclusively from the water column of Lake Huron (via Lake St. Clair), it is likely to contain significantly higher concentrations of algal biomass than the other tributaries. Significant quantities of organic solids may also be attributable to municipal wastewater treatment plant discharges from the extensive urban areas along the Detroit River. While the mean NR-NaOH-P concentration (in µgP/g sediments) varied widely among the other rivers sampled, this fraction comprised a relatively

TABLE 10. MEAN COMPOSITION OF THE NON-APATITE INORGANIC P (NAIP) FRACTION IN TRIBUTARY SUSPENDED SEDIMENTS

Tributary	Mean NAIP (=R-NaOH-P + CDB-P)		Mean ratio of (R-NaOH-P)/(CDB-P)
Maumee River	511 μgP/g sed.	(40.6%)*	1.147
Sandusky River	535	(45.1)	1.257
Cuyahoga River	721	(54.9)	1.575
Honey Creek	559	(47.1)	1.754
Genesee River	357	(37.3)	0.909
Cattaraugus Creek	128	(20.1)	0.561
Detroit River	482	(33.8)	1.723

* Values in parentheses are NAIP expressed as a percentage of T-Sed-P.

constant percentage of T-NaOH-P (from 23.1% for Cuyahoga River sediments to 39.4% for Cattaraugus Creek). So, there appears to be a positive correlation between the amount of organic material present in association with tributary suspended sediments and the magnitude of _both_ the NR-NaOH-P and R-NaOH-P fractions. This is consistent with the findings of Williams _et al_. (1980a), who reported a close correlation between non-apatite and organic forms of P associated with a variety of sediments from the lower Great Lakes basin. It is possible that orthophosphate is adsorbed onto particulate organic matter by relatively weak, physical forces and released in a reactive form during the NaOH extraction (i.e. as R-NaOH-P). Other P may be bound to the organic substances by stronger chemical forces, and released in a non-reactive form (NR-NaOH-P). The R-NaOH-P fraction should be more readily available for algal uptake than the NR-NaOH-P fraction.

Comparison of Results with Previous Studies

The chemical fractionation results obtained in this study may be compared to those reported by Logan (1978) for all tributaries except the Genesee and Detroit Rivers. The mean concentrations of R-NaOH-P and CDB-P (Table 8) were lower than those of Logan (1978) (Table 9) for all rivers. If Logan's one Cuyahoga River sample (with unusually high T-Sed-P) is eliminated from the calculations, his R-NaOH-P and CDB-P values (in μgP/g sed) average 32.6% and 51.4% greater, respectively, than those measured at the same sites in this study. This may be partly due to the fact that the samples analyzed by Logan (1978) were generally collected under conditions of lower flow and suspended solids concentration than those in this study. As mentioned previously, data from Baker (1982a) have shown an increasing trend in T-Sed-P (PP/SS) with decreasing SS. When fractionation results are erpressed as a precentage of T-Sed-P based on analysis of raw river water, the R-NaOH-P and CDB-P concentrations from the two studies are much more consistent. It is also possible that the observed disparity in the chemical fractions between the two studies arises from differences in techniques for concentrating and storing the suspended sediments. The freeze-drying process used by Logan (1978) may have caused sediment particles to fracture, making sediment P more susceptible to removal by the extraction reagents. On the other hand, sediments stored as a concentrate in P-free media may release small amounts of P to solution. This would not be accounted for in any of the chemical fractions as measured in this study.

Closer agreement was obtained with the results of Logan (1978) for the HCl-P and Residual P concentrations. The two studies yielded roughly equivalent quantities of HCl-P for sediments from the Cuyahoga River, Cattaraugus Creek and Honey Creek, while the present study showed lower amounts for the Maumee and Sandusky Rivers. The mean Residual P levels listed in

Table 8 exceeded those of Logan (1978) for the Maumee River, Sandusky River and Honey Creek, but were slightly less for Cattaraugus Creek and the Cuyahoga River.

Analyses on samples from the Sandusky River and Honey Creek by Baker (1982b) yielded mean R-NaOH-P fractions of 23.0% and 22.7% of T-Sed-P, respectively, while the present study showed 25.1% and 30.0% in this fraction for the same sampling sites. It should be noted, however, that the results of Baker (1982b) were for samples collected during periods of higher flow and SS concentration. Armstrong, *et al*. (1979) performed extractions on suspended sediments from the Genesee and Maumee Rivers using a different procedure than applied in this study. The NaOH step was conducted at a higher solution:sediment ratio (2000:1 as opposed to 500:1) and was directly followed by extraction with HCl. This procedure yielded a much higher mean concentration of R-NaOH-P for Maumee River sediments, both in µgP/g sediment and as a percentage of T-Sed-P, than was found in the present study. In fact, the R-NaOH-P levels (in µgP/g sediment) reported by Armstrong *et al*. (1979) for this river averaged only slightly less than the sum of R-NaOH-P and CDB-P listed in Table 8. While R-NaOH-P for the Genesee River, in µgP/g sediment, is comparable for the two studies, it constitutes a greater fraction of T-Sed-P for the samples of Armstrong *et al*. (1979). As expected, the HCl-P fraction proved to be considerably smaller in the present study since this step was preceded by a CDB extraction.

BIOASSAY MEASUREMENTS OF PHOSPHORUS AVAILABILITY FOR TRIBUTARY SAMPLES

First-Order Sediment P Release Coefficients

The release of available P from river sediments in the DCDA reactors was measured by monitoring P uptake by *Selenastrum* in the assay vessel. Plots of cumulative P release versus time obtained from bioassays on two of the samples (#19 and #20) are shown in Figure 8. The form of these release curves is typical of the results observed for the majority of samples analyzed. In Figure 8, the error bars about each data point represent one standard deviation for the triplicate bioassays, while the solid lines illustrate the amount of sediment P release predicted by the first-order equation:

$$P_{rel}(t) = P_{ult}[1 - \exp(-k_r t)] \qquad (10)$$

where $P_{rel}(t)$ = the amount of sediment P released at time t (µgP/g sed), and $P_{ult}(t)$ and k_r are as defined in Equation 7. The equivalency of Equations 7 and 10 is discussed in detail in

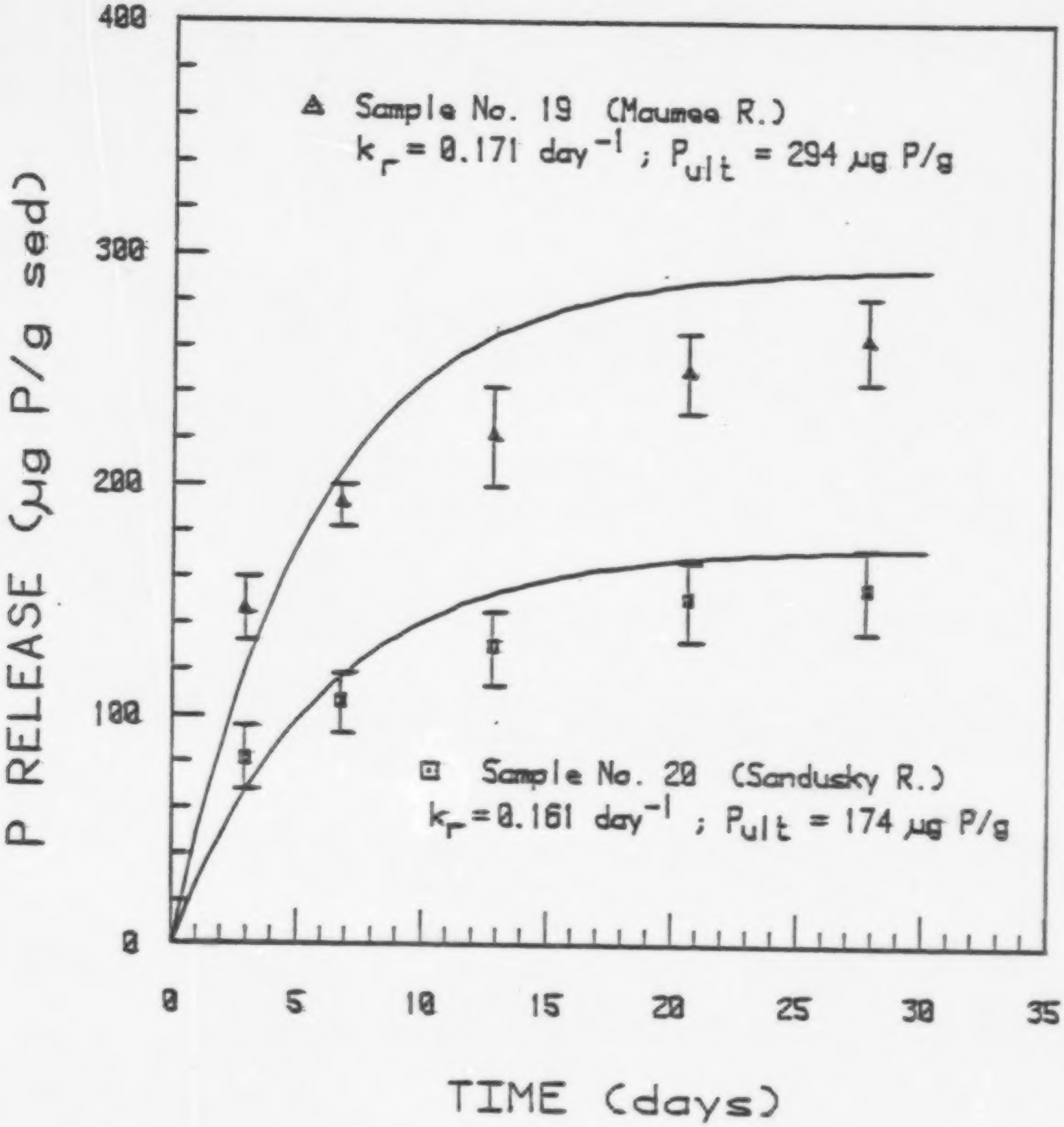


Figure 8. Cumulative release of sediment P versus time measured in DCDA bioassays on Samples #19 (Maumee R.) and #20 (Sandusky R.).

Appendix C. For samples #19 and #20, this equation tends to underpredict the observed P release for approximately the first five days of the DCDA experiments, and to overpredict the results obtained for the remainder of the bioassays. Similar tendencies were noticed for most of the other samples as well. The data suggest that a single first-order mechanism may not be responsible for all of the sediment P release. It is possible that two separate components of available sediment P may be released at different first-order rates. This possibility is discussed in greater detail later in this section.

Values calculated for the first-order release coefficients, P_{ult} and k_r, by the Thomas Method are listed in Table 11 along with means for all tributaries and for 1980 and 1981 samples. P_{ult} is also given as a percentage of the T-Sed-P concentration measured on the sediments placed in the DCDAs. The order of mean bioavailable sediment P concentrations for the tributaries was Cuyahoga > Maumee > Honey Creek > Sandusky > Genesee > Cattaraugus. The mean values of P_{ult} ranged from a low of 38.8 μgP/g sed (7.7% of T-Sed-P) for Cattaraugus Creek to a high of 449.2 μgP/g sed (33.9% of T-Sed-P) for the Cuyahoga River. Mean first-order release rates (k_r) ranged from 0.131 day^{-1} for Cattaraugus Creek to 0.264 day^{-1} for the Genesee River.

Variability of DCDA Results

The variability of the bioassay results was comparable to that observed for the sediment P fractionation data. That is, while significant differences in P_{ult} were seen among samples from a certain tributary, greater variability was generally found between tributaries. The coefficients of variation (C.V.) calculated for P_{ult} in the individual tributaries and for the mean P_{ult} values from all six tributaries are listed in Table 12. The C.V. for the tributary means exceeded that for all of the individual tributaries except Cattaraugus Creek, which contained unusually low levels of bioavailable sediment P. In addition, differences between the mean P_{ult} concentrations for 1980 and 1981 samples (Table 11) for a particular river were small compared to the differences between rivers. The k_r values were much less variable than P_{ult}, both among samples for a particular tributary and between tributaries.

TABLE 11. FIRST-ORDER RELEASE COEFFICIENTS CALCULATED FROM BIOASSAY DATA BY THE THOMAS METHOD

Tributary and sample no.	T-Sed-P* in DCDAs (µgP/g sed)	Sediment P released in DCDAs (µgP/g sed)	Ultimately Bioavailable Sediment P P_{ult} (µgP/g·sed)	P_{ult} as a % of T-Sed-P	Release Rate, k_r (day^{-1})
Maumee River:					
5	1192	300.2	350.2	29.4	0.229
8	1254	203.6	230.6	18.4	0.144
13	1126	165.2	187.3	16.6	0.204
15	1646	529.6	596.2	36.2	0.082
17	1379	406.2	432.3	31.3	0.101
19	1270	262.0	295.3	23.3	0.177
21	1074	172.1	201.3	18.7	0.195
27	1683	530.6	629.3	37.4	0.244
41	1301	248.7	281.6	21.6	0.201
42	1287	183.9	213.3	16.6	0.221
50	1174	267.7	293.2	25.0	0.203
Mean (1980)	1277	291.3	327.6	24.8	0.162
Mean (1981)	1361	307.7	354.3	25.1	0.217
Mean (All)	1308	297.3	337.3	25.0	0.182
Sandusky River:					
2	1253	321.2	352.3	28.1	0.209
7	1144	151.3	164.6	14.4	0.103
11	1136	144.4	163.4	14.4	0.207
16	1018	195.9	218.6	21.5	0.173
20	984	154.9	173.6	17.6	0.165
25	1028	219.6	226.1	22.0	0.105
26	1205	224.1	231.2	19.2	0.140
28	1314	257.0	307.3	23.4	0.191
30	1405	300.6	343.0	24.4	0.160
31	1373	285.0	343.5	25.0	0.067
44	972	158.7	174.1	17.9	0.221
45	1022	216.1	239.6	23.4	0.225
46	1081	218.9	240.2	22.2	0.226

(continued)

TABLE 11 (continued)

Tributary and sample no.	T-Sed-P in DCDAs (µgP/g sed)	Sediment P released in DCDAs (µgP/g sed)	Ultimately Bioavailable Sediment P P_{ult} (µgP/g sed)	P_{ult} as a % of T-Sed-P	Release Rate, k_r (day^{-1})
Sandusky River: (cont'd.)					
47	1109	258.2	273.4	24.7	0.201
49	1174	209.3	225.6	19.2	0.192
51	1092	247.3	271.2	24.8	0.200
52	1152	227.5	253.6	22.0	0.221
Mean (1980)	1094	197.9	216.4	19.7	0.160
Mean (1981)	1173	236.6	263.9	22.4	0.186
Mean (All)	1145	222.9	247.1	21.4	0.177
Cuyahoga River:					
1	1294	340.6	383.5	29.6	0.231
4	1334	569.5	645.5	48.4	0.189
12	1210	261.3	279.8	23.1	0.145
29	1419	421.9	487.8	34.4	0.189
Mean (1980)	1279	390.5	436.3	33.7	0.188
Mean (1981)	1419	421.9	487.8	34.4	0.189
Mean (All)	1314	398.3	449.2	33.9	0.188
Genesee River:					
3	900	141.9	173.8	19.3	0.264
Cattaraugus Creek:					
6	362	53.7	61.9	17.1	0.172
9	562	0.0	0.0	0.0	–
10	612	0.0	0.0	0.0	–
22	648	24.4	27.6	4.3	0.177
23	610	79.3	104.5	17.1	0.043
Mean (All)	559	31.5	38.8	7.7	0.131

(continued)

TABLE 11 (continued)

Tributary and sample no.	T-Sed-P* in DCDAs (µgP/g sed)	Sediment P released in DCDAs (µgP/g sed)	Ultimately Bioavailable Sediment P P_{ult} (µgP/g sed)	P_{ult} as a % of T-Sed-P	Release Rate, k_r (day^{-1})
Honey Creek:					
32	1337	297.9	346.5	25.9	0.224
33	1383	279.0	320.7	23.2	0.212
43	1094	262.6	284.2	26.0	0.199
48	978	211.3	240.8	24.6	0.223
Mean (All)	1198	262.7	298.0	24.9	0.214

* The T-Sed-P values listed in this table are based on TP and SS analyses performed on the sediment suspensions placed in the DCDAs.

TABLE 12. COEFFICIENTS OF VARIATION FOR P_{ult} MEASURED BY DCDA BIOASSAYS

Values included	Coefficient of variation for: P_{ult} in µgP/g sed	P_{ult} as a % of T-Sed-P
Maumee River samples	45.5%	30.4%
Sandusky River samples	25.0%	17.8%
Cuyahoga River samples	34.7%	31.7%
Cattaraugus Creek samples	115.2%	113.7%
Honey Creek samples	15.4%	5.3%
Means for all rivers	54.9%	39.1%

The bioassay and chemical fractionation data collected in this study indicate that many of the characteristics (e.g. chemical form and biological availability) of sediment P transported by storm runoff events do not vary substantially over the course of a year or from year to year. Instead, these characteristics appear to remain relatively constant for a particular set of soil and land use conditions. This observation has important implications regarding efforts to characterize the bioavailability of sediment P inputs to a lake basin. In cases where it is not possible to perform bioassay or chemical fractionation measurements on sediments from all streams in the basin, it may be reasonable to assume similiar behavior for sediment P transported by several streams within a large, geographically distinct region.

Comparison with Previous Bioassay Studies

The shape of the sediment P release curves observed in this study is similar to that reported by other researchers using bioassay techniques with repetitive sampling (e.g. Hegemann et al., 1982; Verhoff, et al., 1978). The release of P from sediments occurred more rapidly than in previous studies utilizing direct contact between algae and sediments. This is most likely due to the fact that the bioassay reactors employed by Hegemann et al. (1982) and Verhoff et al. (1978) did not receive continuous mixing, while the sediments and algae in the DCDAs did.

Although the DCDA bioassay procedure differs markedly from most of the methods used in past investigations, some of the results are quite comparable. For example, Verhoff et al. (1978) found that about 20-25% of total P was removed by algae from Honey Creek suspended sediments during 80-day incubations, while Cattaraugus Creek sediments supported negligible algal growth. Both of these findings are consistent with the bioassay results of the present study. However, the mean P_{ult} value of 21.4% of T-Sed-P calculated from DCDA bioassay data on Sandusky River sediments is considerably greater than the 6-7% release measured by Verhoff et al. (1978) for this river. Dorich et al. (1980) reported an average release of 20.7% of T-Sed-P for storm runoff sediments collected from Black Creek, a tributary to the Maumee River. This agrees fairly well with the mean P_{ult} value of 25.0% obtained for the Maumee River in this study. Bioassays conducted by Williams et al. (1980a) on suspended sediments from Oakville and Hillman Creeks in Ontario, Canada (tributaries to the Lower Great Lakes) yielded estimates of 24% and 37% of T-Sed-P, respectively, as available for algal uptake. Considering that these values were obtained using incubation periods of only 12 days (Oakville Creek) and 18 days (Hillman Creek), they would appear to fall at the high end of the range of bioavailabilities observed in the present study. On the other hand, Cowen and Lee (1976b) reported that less than 6% of particulate P in Genesee

River water was available to *Selenastrum*, while 15.8% was released in the DCDA bioassays and P_{ult} was estimated at 19.3% of T-Sed-P in this study. In general, the results presented in Table 11 tend to agree more closely with those of previous studies that utilized a direct mesurement of algal uptake of P than those that relied upon cell counts to estimate P uptake.

Two-Component Release Coefficients

As was mentioned previously, attempts to describe the release of sediment P in the DCDAs by a single first-order expression resulted in an underprediction of the observed results early in the bioassays and overprediction later in the runs. In order to achieve a better fit with the DCDA data, an investigation was conducted into the possibility that two separate components of sediment P were released at different first-order rates. Logan *et al.* (1979) have suggested that R-NaOH-P may be released at a more rapid rate than CDB-extractable sediment P. Such a release may be described mathematically by the equation:

$$P_{rel}(t) = P_r[1-\exp(-k_{rr}t)] + P_s[(1-\exp(-k_{sr}t)] \qquad (11)$$

where P_r, P_s = the amount of sediment P released (in μgP/g sed) via the rapid and slow mechanisms, respectively

and k_{rr}, k_{sr} = the first-order rates for the rapid and slow release mechanisms, respectively (day^{-1}).

By substituting this expression into mass-balance equations for P in both vessels of the DCDAs, an expression was also obtained for the concurrent uptake of P by algae on the assay side of the DCDAs as a funciton of time.

A computer algorithm was developed to calculate the four release coefficients in Equation 11 based on optimization of the correlation between observed and predicted values of P uptake. Application of this algorithm to the bioassay results yielded values of the rapid component release rate, k_{rr}, in excess of 1.0 day^{-1} for roughly half of the samples. Since this rate is on the same order as the bulk diffusion rate measured for the DCDA reactors ($\alpha = 2.065\ \text{day}^{-1}$), the accuracy with which k_{rr} can be quantified by this method is questionable. However, precise estimation of k_{rr} may not be essential, inasmuch as these preliminary calculations indicate that the time required for the release of most of the "rapid component" of sediment P is considerably shorter than the expected residence time of the suspended sediments in the water column of the receiving lake.

It was decided that, for all practical purposes, the rapid component could be considered to be released from the sediments essentially instantaneously upon entering the water column (or the DCDAs). In this case, the release of sediment P can be described by the equation:

$$P_{rel}(t) = P_r + P_s[(1-\exp(-k_{sr}t)] \qquad (12)$$

Using a mass-balance approach, the following expression was derived for the corresponding uptake of P on the assay side of the DCDAs:

$$Q_2(t) = \frac{\alpha P_s}{(\alpha-k_{sr})}[1-\exp(-k_{sr}t)] - \frac{k_{sr}P_s}{(\alpha-k_{sr})}[1-\exp(-\alpha t)] + P_r[1-\exp(-\alpha t)] \qquad (13)$$

where $Q_2(t)$ = cumulative P uptake by algae on assay side (in µgP/g sed) at time t.

The derivation of this equation is presented in Appendix E. Again, a computer algorithm was developed to calculate values of P_r, P_s, and k_{sr} based on the bioassay data. A listing of the BASIC computer program used is also presented in Appendix, E. The release coefficients obtained for each of the samples bioassayed are presented in Table 13. Values are also tabulated for the total amount of sediment P that would ultimately be released ($P_{ult} = P_r + P_s$), along with mean values of all parameters for the individual tributaries.

The mean value calculated for the rapidly released component of sediment P (P_r) was considerably smaller than the mean of the slowly released component (P_s) for all of the rivers except the Genesee. Although P_r comprised 95.2% of P_{ult} for the one Genesee

TABLE 13. TWO-COMPONENT RELEASE COEFFICIENTS (FOR EQUATION 12) CALCULATED FROM DCDA BIOASSAY RESULTS

Tributary and sample number	Total ultimate sediment P release, P_{ult} (μgP/g sed)	Rapidly released component, P_r (μgP/g sed)	Slowly released component, P_s (μgP/g sed)	Release rate for slow component, k_{sr} (day^{-1})
Maumee River				
5	301.2	117.6	183.6	0.261
8	206.6	66.4	140.2	0.122
13	176.2	44.2	132.0	0.101
15	599.6	1.2	598.4	0.076
17	457.2	2.1	455.1	0.077
19	273.0	67.5	205.5	0.105
21	177.1	55.3	121.8	0.118
27	562.6	267.8	294.8	0.096
41	252.7	51.3	201.4	0.164
42	186.9	66.5	120.4	0.156
50	301.7	110.5	191.2	0.084
Mean	317.7	77.3	240.4	0.124
Sandusky River				
7	162.3	29.4	132.9	0.081
11	156.4	20.0	136.4	0.099
16	198.9	13.3	185.6	0.163
20	162.9	56.7	106.2	0.096
25	270.6	9.0	261.6	0.057
26	259.1	33.7	225.4	0.060
28	263.0	140.2	122.8	0.112
30	308.6	154.9	153.7	0.106
31	332.0	0.9	331.1	0.070
44	175.7	67.7	108.0	0.086
45	250.1	81.8	168.3	0.078
46	267.9	104.6	163.3	0.057

(continued)

TABLE 13 (continued)

Tributary and sample number	Total ultimate sediment P release, P_{ult} (µgP/g sed)	Rapidly released component, P_r (µgP/g sed)	Slowly released component, P_s (µgP/g sed)	Release rate for slow component, k_{sr} (day^{-1})
Sandusky River (cont'd.)				
47	337.2	95.2	242.0	0.053
49	256.3	92.1	164.2	0.061
51	276.3	115.6	160.7	0.083
52	259.5	131.7	127.8	0.067
Mean	246.0	71.7	174.4	0.083
Cuyahoga River				
4	573.5	75.2	498.3	0.227
12	278.3	28.3	250.0	0.106
29	433.9	7.5	426.4	0.117
Mean	428.6	37.0	391.6	0.150
Genesee River				
3	142.9	136.0	6.9	0.0917
Cattaraugus Creek				
6	54.7	43.9	10.8	0.119
22	25.4	10.0	15.4	0.0968
23	198.4	0.1	198.3	0.0177
Mean	92.8	18.0	74.8	0.078
Honey Creek				
32	299.9	49.1	250.8	0.196
33	281.0	37.0	244.0	0.196
43	284.6	75.9	208.7	0.106
48	213.3	21.6	191.7	0.214
Mean	269.7	45.9	223.8	0.178

River sample, this component averaged only 8.6 to 29.1% of P_{ult} for the other tributaries. The mean values of P_{ult} obtained using the two-component algorithm were less than the mean P_{ult} calculated by the Thomas Method for the Maumee, Cuyahoga, and Genesee Rivers and Honey Creek, but were greater for the Sandusky River and Cattaraugus Creek. Also, as expected, the tributary means for the slow component release rate (k_{sr}) were all substantially lower than the mean Thomas Method release rates (k_r in Table 11).

A correlation coefficient matrix containing all of the one-component and two-component release parameters is presented in Table 14. The values of P_{ult} calculated by the two different methods were closely correlated. Fluctuations in P_{ult} appear to be associated with changes in the slowly released component (P_s) rather than the rapidly released component (P_r). However, the overall rate of sediment P release is influenced by the size of the rapidly released component, as evidenced by the fairly strong correlation between P_r and k_r. Although the slow component release rate (k_{sr}) also showed a significant correlation with k_r, the relationship was not as close as that between P_r and k_r.

It should be noted that, since the sediment P release curves obtained from bioassay experiments consisted of only four or five data points, there is a good deal of uncertainty involved in the calculation of the two-component release coefficients. Nevertheless, there seems to be some potential for improving the description of sediment P release using the two-component approach. In an effort to gain further insights into the mechanisms of sediment P release, the two-component release coefficients were included in the analyses presented in the following subsections.

Comparison of Sediment P Release Models

The amount of particulate phosphorus becoming available for algal uptake while river sediments are suspended in the water column of the receiving lake depends primarily upon the relative rates of P release and settling of particles from the water column. The western basin of Lake Erie, for example, has a mean depth of about 7.3 m and a mean hydraulic retention time of about

TABLE 14. SIMPLE CORRELATION COEFFICIENT MATRIX FOR ONE-COMPONENT AND TWO-COMPONENT SEDIMENT P RELEASE COEFFICIENTS

	P_r	P_s	P_{ult} $(=P_r+P_s)$	k_{sr}	P_{ult} (one-comp.)	k_r
P_r	1.0000* 0.0000	-0.2306 0.1637	0.2147 0.1956	0.0129 0.9387	0.2754 0.0942	0.5836 0.0001
P_s		1.0000 0.0000	0.9009 0.0001	0.0830 0.6203	0.8433 0.0001	-0.3886 0.0159
P_{ult} $(=P_r+P_s)$			1.0000 0.0000	0.0891 0.5949	0.9693 0.0001	-0.1297 0.4378
k_{sr}				1.0000 0.0000	0.2674 0.1046	0.4134 0.0099
P_{ult} (one-comp.)					1.0000 0.0000	0.0266 0.8704
k_r						1.0000 0.0000

* Top value is the simple correlation coefficient (r). Bottom value is α, the probability of Type I error (i.e., rejection of a true null hypothesis, H_o: $\rho=0$).

1.5 months. Measurements performed in this study (presented later in this section) indicate that sediment particles entering the western basin from the Maumee River during high flow events have a volume-weighted median particle diameter of approximately 3 μm. Assuming a spherical particle geometry and a uniform density of 2.5 g/cm^3, Stoke's Law predicts that 50 percent of the particle mass would settle into the bottom sediments within about 10 days. Although this is a rather crude estimate of sediment removal rate, comparison with available phosphorus release rates measured in this study indicates that tributary suspended sediments will probably settle to the lake bottom or be transported a considerable distance before all of the potentially available phosphorus has been released. It seems essential, therefore, that dynamic water quality models properly account for the rate at which allochthonous particulate P is made available in the water column of a lake.

Most deterministic nutrient-phytoplankton models currently being applied to the Great Lakes do include a mechanism for the conversion of allochthonous "unavailable" P to available P (Thomann, _et al_., 1975; Bierman, _et al_., 1980; DiToro and Matystik, 1980; DiToro and Connolly, 1980; Rodgers and Salisbury, 1981). However, particulate P inputs from tributary sources are usually lumped together with P present in decomposing aquatic organisms (e.g. phytoplankton, zooplankton) in the water column to make up the total "unavailable" P pool. As illustrated in Figure 8, the data collected in this study suggest that the rate of release of available P from tributary suspended sediments may be represented as a first-order function of the amount of potentially available phosphorus remaining on the sediments. On the other hand, in the models currently employed, the rate of release is considered to be a first-order function of the total particulate P remaining in the "unavailable" pool. No distinction is made between the rate of conversion of allochthonous "unavailable" P (primarily inorganic sediment P) and the rate of conversion of autochthonous "unavailable" P (primarily algal-bound P) in these models. The rate coefficients used to characterize release from the "unavailable" P pool are generally lower than those measured for tributary sediments in this study (Table 11).

A comparison of the two approaches to predicting the cumulative P release from tributary sediments, applied to sample #19 (Maumee River), is presented in Figure 9 along with the DCDA data. Using the one-component release coefficients calculated by the Thomas Method (Table 11) the predicted release of available P versus time would be given by the equation:

$$P_{rel}(t) = 295.3\ [1-\exp(-0.177t)] \qquad (14)$$

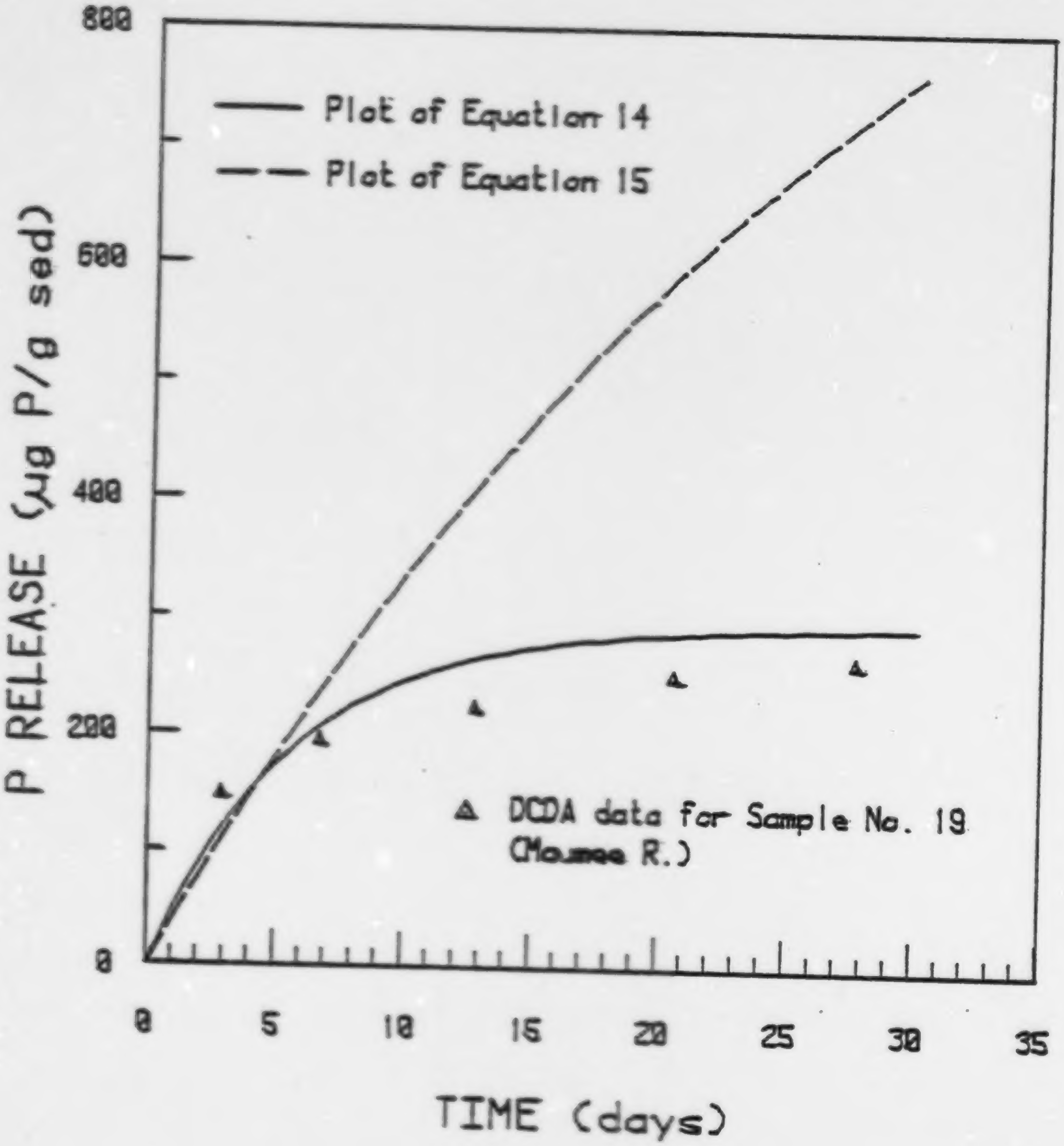


Figure 9. Comparison of current Great Lakes model predictions of P_{rel} versus time with actual bioassay data and the one-component model predictions for Sample #19.

where $P_{rel}(t)$ = the cumulative available P released from the sediments (μgP/g sed).
295.3 = ultimately available sediment P calculated for Maumee River sample #19 (μgP/g sed).
0.177 = available P release rate calculated for sample #19 (day^{-1}).
t = incubation time of sediments in the lake water column (days).

Assuming a water temperature of 20 °C in a highly productive systems such as Lake Erie, the approach used by DiToro and Connolly (1980) would result in the following equation for predicting available P release from sample #19 sediments:

$$P_{rel}(t) = 1286\ [1-\exp(-0.03t)] \tag{15}$$

where 1286 = the total particulate P concentration of Maumee River sample #19 sediments (μgP/g sed) (Table 8)
and 0.03 = the rate of conversion of "unavailable" P to available P at 20 °C (day^{-1}).

These two equations provide similar predictions for the first 5-7 days. Thereafter, however, Equation 15 predictions exceed both the observed data and the predictions of Equation 14 by a considerable amount. Virtually all of the samples analyzed in this study behaved in a manner similar to sample #19 when the two methods for predicting sediment P release were compared. The deviation between the two methods is primarily a function of the difference between the amounts of total particulate P and ultimately available sediment P.

The implications of the above analysis are quite obvious. For systems in which the tributary sediments do not reside long in the water column (less than about 7 days), either Equation 14 or 15 would yield reasonable results. On the other hand, when tributary sediments remain suspended in the water column for longer than about 7 days, the current modeling approach (Equation 15) would tend to overestimate the input of soluble P to the lake. For models calibrated primarily on the basis of algal biomass, this would be likely to cause an overprediction of soluble P concentrations in the water column. In turn, this might lead to either an overestimation of the phosphorus retention time, or an unrealistic adjustment of other model coefficients in order to effect a calibration. It might also lead to inaccurate conclusions about the relative contributions of the various phosphorus sources to biological productivity in the lake.

As was mentioned previously, a third possible approach to the prediciton of P release from tributary sediments is the use of a two-component release expression such as Equation 12. Substituting the release coefficients calculated for sample #19 (Table 13) into this equation yields:

$$P_{rel}(t) = 67.5 + 205.5\ [1-\exp(-0.105t)] \qquad (16)$$

where 67.5 = the amount of rapidly released sediment P calculated for Maumee River sample #19 (μgP/g sed).

205.5 = the amount of slowly release sediment P calculated for sample #19 (μgP/g sed).

0.105 = the first-order rate coefficient for the slowly released component (day^{-1}).

A comparison between the predictions of this equation and Equation 14 is presented in Figure 10, superimposed on the observed sediment P release data from bioassays on sample #19. The predictions of the two-component equation show a slightly better agreement with the observed data than those based on the first-order function of ultimately available sediment P. Equation 16 corresponds almost exactly to the observed P release at times greater than about 10 days. However, as with Equation 14, the predictions fall below the DCDA data during the early portion of the incubations. It is possible that a more accurate quantification of the two-component release coefficients could be achieved if the DCDAs were sampled more frequently, especially during the first week of the bioassays.

Although close agreement with the bioassay data is certainly important, that alone is not necessarily justification for adopting a particular model of sediment P release over others. It is also desirable to establish a connection between the model coefficients and the physical, chemical and biological characteristics of the sediments. That is, evidence should exist to indicate that the model provides a description of the actual mechanisms of sediment P release. In this way, it may be possible to estimate the model coefficients based on certain characteristics of the sediments. An investigation into relationships between the coefficients calculated for one- and two-component sediment P release (Tables 11 and 13) and the various chemical measurements performed on the same samples (Table 8) is presented later in this section.

Bioavailability of Soluble P in Tributaries

A sizable portion of the total phosphorus input to the Lower Great Lakes via diffuse sources is in soluble rather than

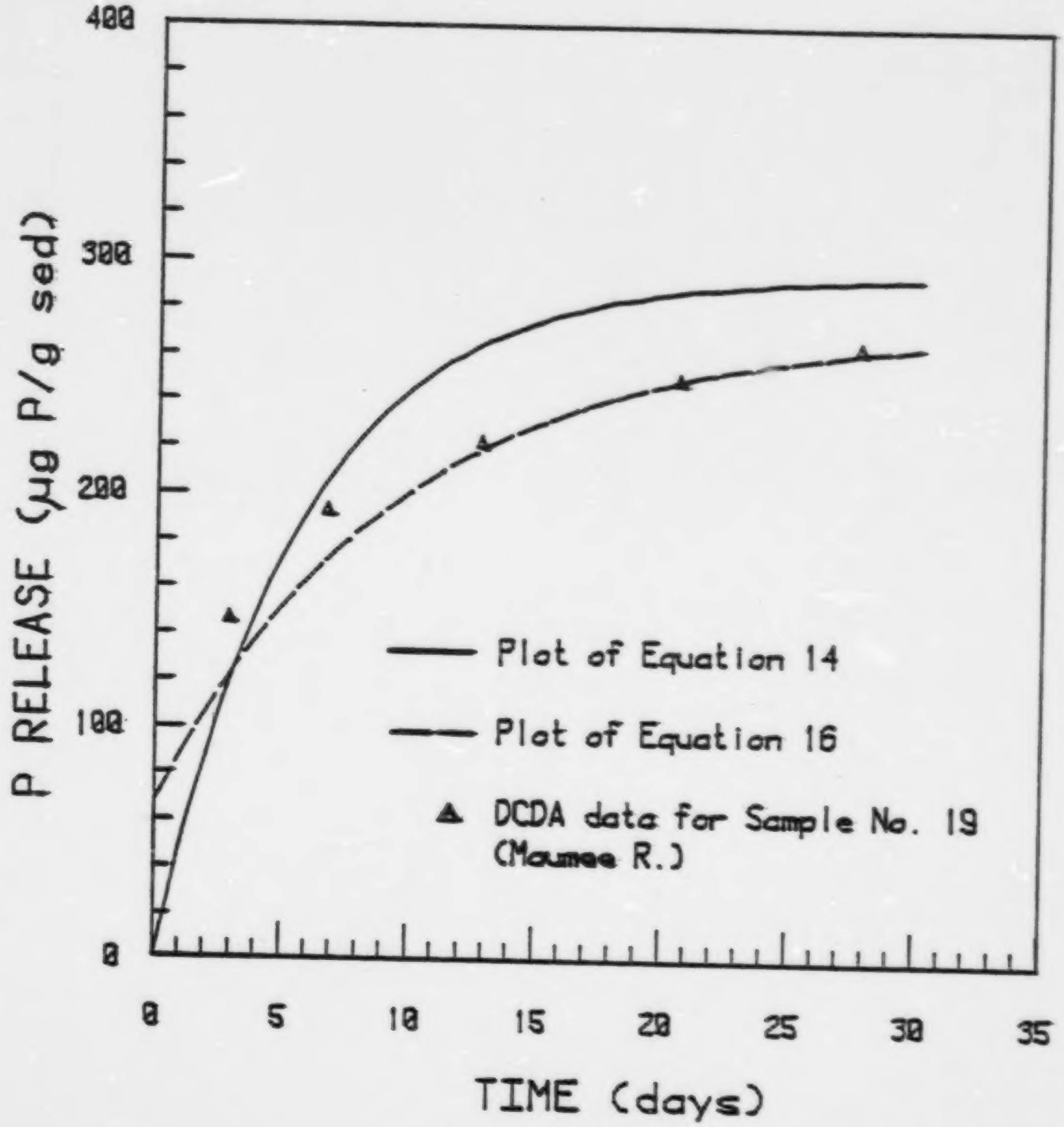


Figure 10. Comparison of one-component (Eqn. 14) and two-component (Eqn. 15) sediment P release models with bioassay data for Sample #19.

particulate form. Based on loading data provided by the U.S. Army Corps of Engineers, Buffalo District, Salisbury et al. (1983) indicated that SRP comprised about 25% of the tributary total P load to Lake Erie (excluding the Detroit River load) for the years 1970-80. This component is generally considered to be readily available for uptake by algae or other aquatic organisms. Bioassays were conducted on several of the tributary samples collected in this study to measure the availability of soluble P forms to *Selenastrum*. The results are presented in Table 15. Over 90% of SRP was found to be available within 24 hours for all samples except those from Cattaraugus Creek. The algal inoculum rapidly reduced SRP to a nearly constant level (usually from 2 to 5 µg/l) regardless of the initial concentration present. This factor, in combination with an unusually low initial soluble P content, accounts for the low percentage utilized by the algae for Cattaraugus Creek samples.

TSP showed a slightly lower degree of availability than SRP for most of the samples analyzed. This was expected, since the TSP fraction includes non-reactive forms of phosphorus that may not be utilized by algae as readily as soluble orthophosphate. Although most of the TSP uptake occurred during the first 24 hours of incubation, several samples showed additional reductions in this fraction at the second sampling (4 to 6 days of incubation). Thus, it appears that a small portion of the soluble P, although not immediately available, may be broken down into an assimilable form within a few days following exposure to an active P-starved algal population. The TSP concentration in some of the bioassay reactors increased between the first and second samplings. This occurred only when the algae were not harvested (removed by filtering) after 24 hours, and may have resulted from the excretion of organic compounds containing P by the algal cells following a period of rapid growth and P uptake. A third sampling at 12-14 days was included in several of the soluble P bioassay experiments. However, this did not reveal any further decreases in TSP. As with SRP, the algal inoculum reduced TSP to a relatively constant level (4-8 µg/l) regardless of the initial concentration present in the tributary sample. Since the samples from the Ohio rivers contained high levels of TSP, in most cases, 90% or more was found to be bioavailable. Soluble P concentrations were lower for samples from the New York rivers, and as a result, the fraction taken up by *Selenastrum* was also smaller.

TABLE 15. BIOAVAILABILITY OF SOLUBLE PHOSPHORUS IN TRIBUTARY SAMPLES

Tributary	Sample number	Initial conc. (µg/ℓ)		Conc. after 24 hr incubation (µg/ℓ)		Conc. at 4-6 days (µg/ℓ)	% available	
		TSP	SRP	TSP	SRP	TSP	TSP	SRP
Maumee River	5	133.3	109.4	7.6	2.9	13.1	94.3	97.3
	8	97.5	88.2	7.7	3.8	11.2	92.1	95.7
	13	102.5	93.1	8.4	3.8	4.3	95.8	95.9
	Mean	111.1	96.9	7.9	3.5	9.5	94.1	96.3
Sandusky River	2	129.0	99.9	14.8	2.8	7.4	94.3	97.2
	7	91.5	83.3	7.2	4.8	10.2	92.1	94.2
	11	77.4	59.2	5.8	3.6	5.1	93.4	93.9
	16	97.3	83.9	10.6	4.0	6.7	89.1	95.2
	Mean	98.8	81.6	9.6	3.8	7.3	92.2	95.1
Cuyahoga River	1	39.5	32.1	19.1	2.5	10.4	73.7	92.2
	4	51.4	30.7	4.0	0	12.8	92.2	100
	12	75.3	47.8	7.5	3.9	6.4	91.5	91.8
	Mean	55.4	36.9	10.2	2.1	9.9	85.8	94.7
Cattaraugus Creek	6	11.4	11.4	3.1	3.1	6.2	72.8	72.8
	9	14.6	4.2	11.9	3.6	10.4	28.8	14.3
	10	10.8	3.9	5.4	3.4	5.6	50.0	12.8
	Mean	12.3	6.5	6.8	3.4	7.4	50.5	33.3
Genesee River	3	37.0	18.3	9.6	0	6.9	81.4	100

CORRELATIONS BETWEEN CHEMICAL FRACTIONATION AND BIOASSAY RESULTS

Correlations With One-Component Release Coefficients

Simple product-moment correlation coefficients (r) were determined between all chemically-extractable sediment P fractions (Table 8) and the one-component P release coefficients, P_{ult} and k_r (Table 11). The results are listed in Table 16 along with values of α (the probability of rejecting a true null hypothesis, H_o: $\rho=0$). All of the chemical fractions except Residual P were significantly correlated ($\alpha < 0.05$) with P_{ult}. The highest correlation coefficient obtained was between P_{ult} and non-apatite inorganic P (NAIP = R-NaOH-P + CDB-P). The only parameter significantly correlated with k_r was Residual P, although the relationship was not a strong one ($r = 0.3480$, $\alpha = 0.0323$).

The high degree of correlation observed between T-Sed-P and P_{ult} has limited applicability beyond the scope of this study. Total phosphorus in suspended sediments from natural systems is, typically, not a single, uniform substance. Rather, it consists of several components that differ in their proportions and in their relative availabilities. In particular, the results of Table 16 indicate that the inorganic component of base-extractable sediment phosphorus (i.e. R-NaOH-P) is more closely linked to bioavailability than any other single chemical fraction measured in this study. Other authors (Sagher, 1976; Williams, *et al.*, 1980a) have reported the same finding for particulate matter from a variety of sources, although different chemical extraction procedures were used.

In addition to R-NaOH-P, the CDB-P fraction, and to a lesser extent, NR-NaOH-P also appear to contribute to bioavailable sediment P. It is possible, however, that intercorrelations between these fractions magnified the apparent relationships with ultimately available P (P_{ult}). R-NaOH-P displayed a fairly strong correlation with both CDB-P ($r = 0.6285$) and NR-NaOH-P ($r = 0.6111$).

The association between a chemical fraction and available P may be examined independently by mathematically partialling out the effects of these intercorrelations. This was done for the three fractions under discussion and the results are given in Table 17. The partial correlation coefficients between P_{ult} and the non-apatite inorganic fractions (R-NaOH-P and CDB-P) were

TABLE 16. SIMPLE CORRELATION COEFFICIENTS BETWEEN ONE-COMPONENT SEDIMENT P RELEASE COEFFICIENTS AND CHEMICAL FRACTIONS FOR TRIBUTARY SUSPENDED SEDIMENTS

Chemical fraction	One-component release coefficients	
	P_{ult}	k_r
T-Sed-P	r = 0.8006 α = 0.0001	0.1446 0.3862
T-NaOH-P	0.8084 0.0001	0.1610 0.3341
R-NaOH-P	0.7790 0.0001	0.1639 0.3255
NR-NaOH-P	0.6487 0.0001	0.1040 0.5344
CDB-P	0.7229 0.0001	-0.0509 0.7679
HCl-P	-0.3160 0.0470	-0.1690 0.3104
Residual P	0.2182 0.1761	0.3480 0.0323
NAIP(R-NaOH-P + CDB-P)	0.8317 0.0001	0.0885 0.6079

TABLE 17. PARTIAL CORRELATION COEFFICIENTS BETWEEN BIOLOGICALLY AVAILABLE P AND CHEMICAL FRACTIONS FOR TRIBUTARY SUSPENDED SEDIMENTS

Chemical Fraction	One-Component Release Coefficient P_{ult}
R-NaOH-P	0.7407* 0.0001
NR-NaOH-P	0.5454 0.0005
CDB-P	0.7071 0.0001

---

* Top number is partial correlation coefficient. Bottom number is α, the probability of Type I error (i.e., the rejection of a true null hypothesis, $H_o:\rho=0$).

only slightly less than the corresponding simple correlation coefficients. The coefficient between NR-NaOH-P and P_{ult}, on the other hand, showed a more sizable decrease. Thus, R-NaOH-P and CDB-P appear to make significant contributions to bioavailable sediment P, while the contribution of the organic component of base-extractable sediment P (i.e. NR-NaOH-P) may be of minor importance.

The highly significant correlation coefficients seen in Tables 16 and 17 indicate a strong potential for the development of equations to predict the bioavailability parameters, P_{ult} and k_r, based on chemical fractions of sediment P. Linear regression analyses were performed for several pairs of parameters, with P_{ult} or k_r as the dependent variable and the chemical fraction as the independent variable. The regression coefficients obtained are listed in Table 18. As an example, if R-NaOH-P were used to predict ultimately bioavailable sediment P, the appropriate equation would be:

$$P_{ult} = 0.8824\ (\text{R-NaOH-P}) + 17.1 \qquad (17)$$

where P_{ult}, R-NaOH-P, and 17.1 all have units of μgP/g sediment. The regression line corresponding to this equation is superimposed on the tributary sediment data in Figure 11. Comparisons between the regression equations and the observed data are also presented for P_{ult} versus NAIP in Figure 12 and for k_r versus Residual P in Figure 13. From these plots, it is apparent that the amount of sediment P that ultimately becomes available may be predicted from fractionation results with a much greater degree of accuracy than the rate at which this phosphorus is released.

Another possible means of predicting the bioavailability parameters, P_{ult} and k_r, is using an equation based on a linear combination of two or more of the chemical fractions measured. Considering the close correlations between P_{ult} and both R-NaOH-P and CDB-P, a regression analysis was performed to obtain coefficients for a predictive model based on these two fractions. This yielded the following equation:

TABLE 18. SLOPES AND Y-INTERCEPTS FROM LINEAR REGRESSION ANALYSES OF ONE-COMPONENT SEDIMENT P RELEASE PARAMETERS VERSUS CHEMICAL FRACTIONS

Independent Variable	Dependent Variable			
	P_{ult}*		k_r†	
	Slope	y-Int.	Slope	y-Int.
T-Sed-P	0.4383	-238.3		
R-NaOH-P	0.8824	17.1		
CDB-P	1.3622	-42.9		
Residual P			0.0001812	0.1566
NAIP(=R-NaOH-P + CDB-P)	0.6363	-58.0		

[*] y-Intercept values have units of μgP/g sediment. Values of slope are unitless.

[†] y-Intercept values have units of day^{-1}. Values of slope are in $[day^{-1}/(\mu gP/g\ sediment)]$.

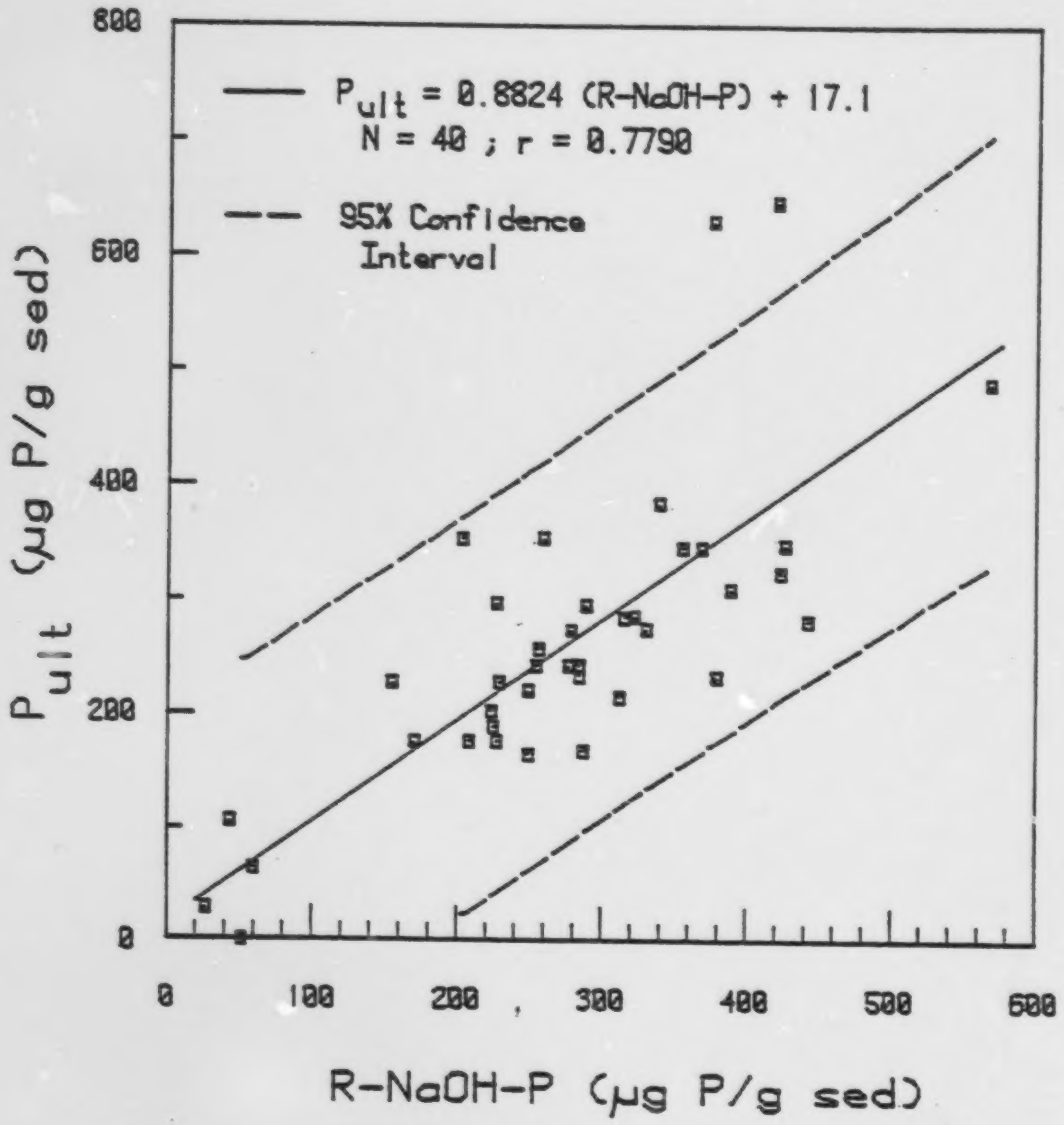


Figure 11. Regression line of P_{ult} versus R-NaOH-P superimposed on data for tributary suspended sediments.

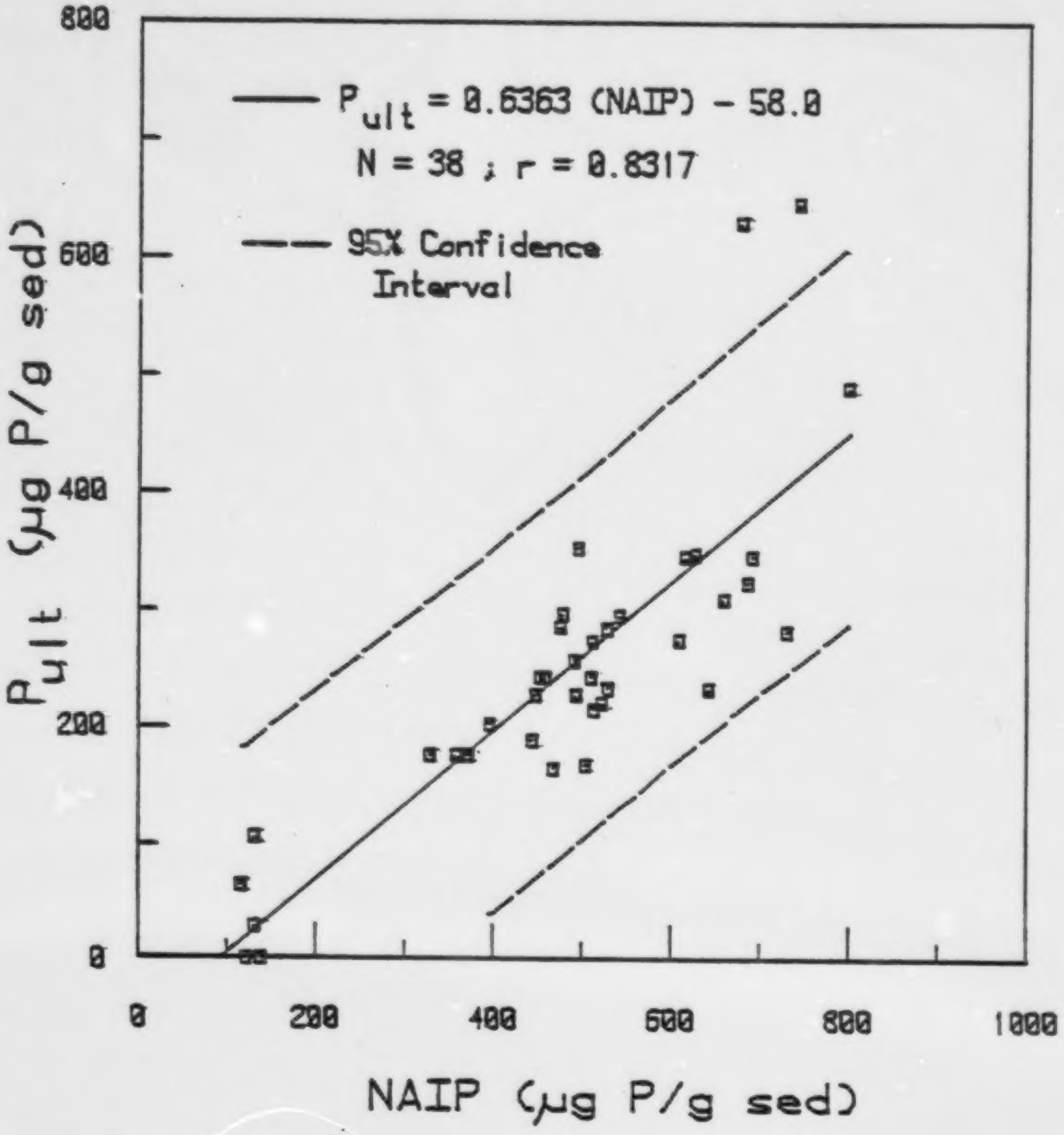


Figure 12. Regression line of P_{ult} versus NAIP (non-apatite inorganic P) superimposed on data for tributary suspended sediments.

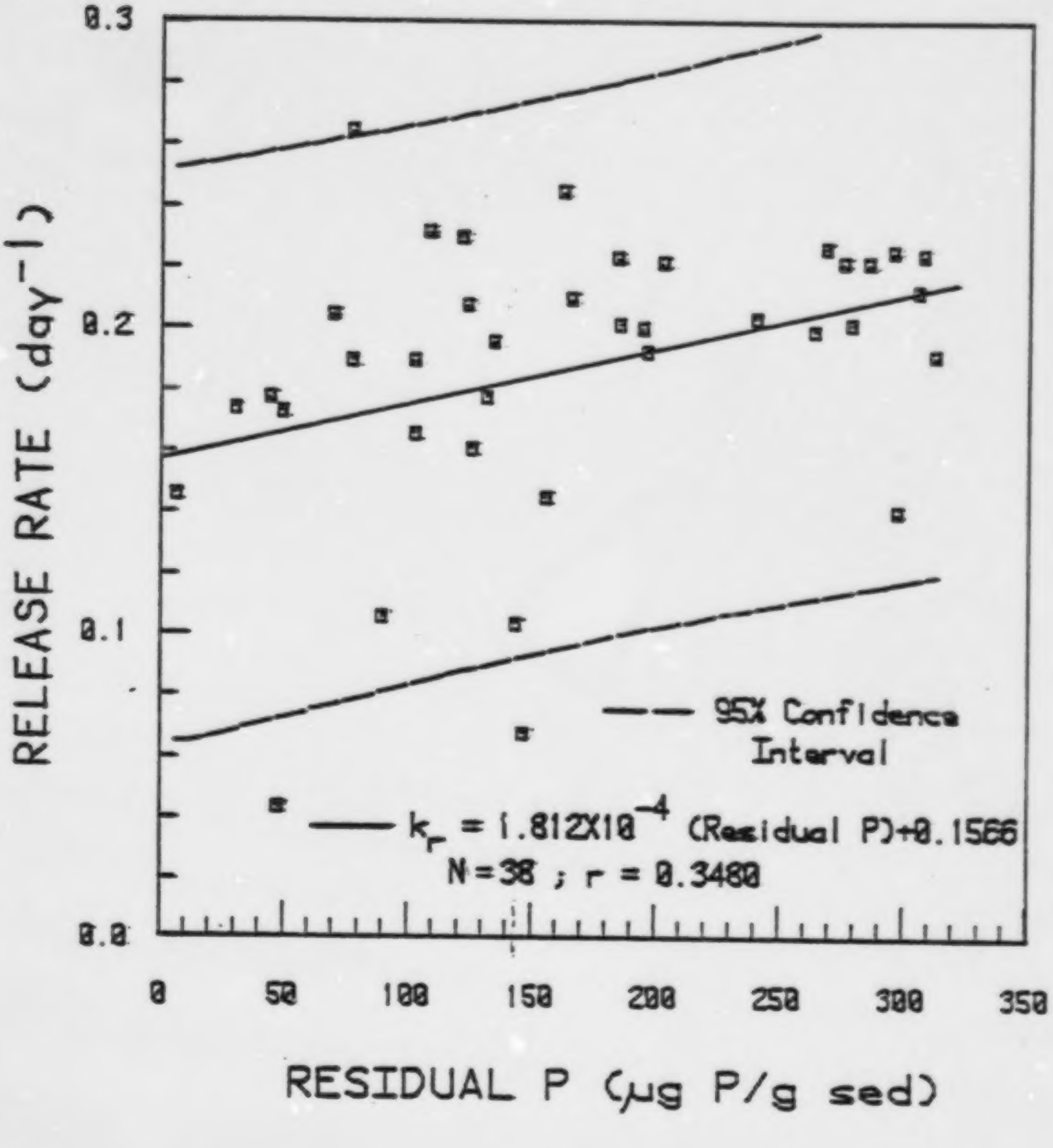


Figure 13. Regression line of k_r versus Residual P superimposed on data for tributary suspended sediments.

$$P_{ult} = 0.6083\ (\text{R-NaOH-P}) + 0.6880\ (\text{CDB-P}) - 61.7 \qquad (18)$$

where, again, all terms have units of μgP/g sediment. The correlation coefficient for this regression was $r = 0.8316$, which is comparable with the highest value found for the regressions involving a single chemical parameter (i.e. $r = 0.8317$ for P_{ult} versus NAIP). From this analysis, it appears that correlation equations based on both the R-NaOH-P and the CDB-P fractions, either alone or summed, provide the most accurate predictions of the ultimate availability of P associated with tributary suspended sediments.

Correlations With Two-Component Release Coefficients

The rationale behind the investigation of a two-component sediment P release model was based on the assertion by Logan *et al*. (1979) that R-NaOH-P represents the short-term available P, while the sum (R-NaOH-P + CDB-P) represents the total sediment P that ultimately becomes available. If this were the case, one would expect a significant correlation between the rapidly released component of bioavailable sediment P (P_r in Table 13) and R-NaOH-P (Table 8) as well as between the slowly released component (P_s) and CDB-P. Simple correlation coefficients were calculated between all of the two-component release coefficients and the chemical fractions for the tributary suspended sediment samples. The results are presented in Table 19.

The correlations observed between P_{ult} ($= P_r + P_s$) and the chemical fractions followed trends similar to those between the one-component parameter, P_{ult}, and these same fractions. Although the correlation coefficients were somewhat lower than in Table 16, P_{ult} nevertheless showed highly significant correlations with all of the fractions listed except HCl-P and Residual P. These correlations appear to be largely attributable to close relationships between the slowly released component (P_s) and several of the chemical fractions. P_s was strongly correlated with CDB-P ($r = 0.6234$), but it was even more closely related to R-NaOH-P ($r = 0.6798$). The rapidly released component of sediment P (P_r) was not significantly correlated with either R-NaOH-P or CDB-P. Based on comparisons with the two-component release coefficients calculated in this study, no evidence was obtained to indicate that the R-NaOH-P and CDB-P fractions

TABLE 19. SIMPLE CORRELATION COEFFICIENTS BETWEEN TWO-COMPONENT SEDIMENT P RELEASE COEFFICIENTS AND CHEMICAL FRACTIONS FOR TRIBUTARY SUSPENDED SEDIMENTS

Chemical fraction	Two-component release coefficients			
	P_r	P_s	$P_{ult}=P_r+P_s$	k_{sr}
T-Sed-P	r=0.3555 α=0.0334	0.5581 0.0004	0.6844 0.0001	0.2790 0.0993
T-NaOH-P	0.2796 0.0986	0.6404 0.0001	0.7211 0.0001	0.2037 0.2335
R-NaOH-P	0.1566 0.3616	0.6798 0.0001	0.6952 0.0001	0.2615 0.1234
NR-NaOH-P	0.4263 0.0095	0.3690 0.0268	0.5483 0.0005	0.0308 0.8584
CDB-P	0.2122 0.2140	0.6234 0.0001	0.6719 0.0001	0.1801 0.2933
HCl-P	-0.1137 0.5089	-0.0979 0.5701	-0.1458 0.3962	-0.0617 0.7209
Residual P	0.2551 0.1332	0.0138 0.9364	0.1403 0.4144	0.0452 0.7936
NAIP (=R-NaOH-P+CDB-P)	0.1978 0.2474	0.7365 0.0001	0.7673 0.0001	0.2577 0.1291

corresponded to rapidly released and slowly released components of bioavailable sediment P, respectively. The correlation coefficients in Table 19 reveal no significant relationship between the release rate for the slow component (k_{sr}) and any of the chemical fractions.

It should be pointed out that even a two-component release model is still a considerable simplifiction of the actual processes controlling sediment P availability. In reality, several different chemical forms of phosphorus may be released at a variety of rates. It is possible that R-NaOH-P and CDB-P were, in fact, released at different rates in the bioassay experiments, but that the sampling schedule and the model chosen did not permit adequate resolution to detect this difference. Further differentiation of bioavailable sediment P into various components would probably require more frequent sampling and a longer incubation period in the DCDAs.

CHANGES IN SEDIMENT P FRACTIONATION DURING DCDA BIOASSAYS

In order to further assess the contributions of the various chemically extractable forms of sediment P to the release observed during bioassays, sediments were reconcentrated after several of the DCDA runs and subjected to the chemical fractionation sequence. The extraction results are presented in Table 20 for the 17 samples analyzed in this manner. Changes in the chemical fractions during the bioassays are tabulated and compared to the measured release of sediment P to *Selenastrum* in Table 21.

The most noticeable feature of the data in Table 21 is that decreases in R-NaOH-P during the bioassays consistently exceeded the changes in all other chemical fractions. A large and relatively constant percentage of the R-NaOH-P initially present in the DCDAs was released for all of the samples analyzed. This percentage ranged from 66.0 to 80.1%, with a mean of 70.8% and a coefficient of variation of only 6.5%. In addition, ΔR-NaOH-P was very closely correlated ($r = 0.896$) with the amount of sediment P taken up by the assay culture in the bioassays. This relationship is shown graphically in Figure 14.

The mean values calculated for the changes in the other fractions all showed average decreases of less than 20 μgP/g sed (and less than 10% of the initial concentration), compared with a mean decrease of 233 μgP/g sed for R-NaOH-P. In general, small decreases in both NR-NaOH-P and HCl-P were observed during the bioassays, although a few samples exhibited small increases in one or the other of these fractions. On the other hand, ΔCDB-P and Residual-P were much more variable. Both of these fractions showed sizable increases for some samples and sizable decreases for others, although on the average, the changes were small. The occasional increases measured in the CDB-P and Residual P

TABLE 20. POST-BIOASSAY SEDIMENT P FRACTIONATION RESULTS

Tributary and sample number	T-Sed-P (µgP/g sed)		Sediment P fractions (µgP/g sed)			
		R-NaOH-P	NR-NaOH-P	CDB-P	HCℓ-P	Residual P
Maumee River						
41*	925	102	114	131	131	278
42*	925	102	114	131	131	278
50	912	85	108	219	84	198
Sandusky River						
26	1,069	128	121	192	120	406
28	1,123	116	135	223	108	446
44	781	63	103	216	54	202
45	814	57	99	216	46	196
46	815	64	110	220	48	204
47	880	81	127	216	68	214
49	832	76	124	259	43	176
51	894	85	133	240	44	177
52	901	87	117	245	45	185
Honey Creek						
32	901	118	135	127	68	288
33	997	122	140	131	74	302
43	792	100	104	223	34	205
48	787	86	118	180	27	159
Cuyahoga River						
29	1,007	113	109	231	153	228

* In order to provide enough sediment for duplicate chemical fractionations, sediments from samples #41 and #42 were combined into the same sediment concentrate after bioassays. Since the sediment chemistries of these two samples were similar, it is felt that the post-DCDA fractionation results obtained are representative of both samples.

TABLE 21. CHANGES IN CHEMICAL FRACTIONATION OF SEDIMENT P DURING DCDA BIOASSAYS COMPARED WITH P RELEASE MEASURED IN DCDAs

Tributary and sample number	Changes in extractable sediment P fractions (μgP/g sed)*							Sediment P release measured in DCDAs	1st Order release rate (days^{-1})
	ΔT-Sed-P	ΔR-NaOH-P	ΔNR-NaOH-P	ΔCDB-P	ΔHCl-P	ΔResidual-P	Σ(ΔFrac.)[†]		
Maumee River									
41	-280(23.2)	-213(67.6)	- 9(7.3)	-80(37.9)	+ 8(6.5)	0	-294(28.0)	249	0.201
42	-333(26.4)	-210(67.3)	- 2(1.7)	-74(36.1)	-64(32.8)	+ 3(1.1)	-347(31.5)	184	0.221
50	-237(20.6)	-204(70.6)	- 9(7.7)	-33(13.1)	- 3(3.4)	- 42(17.5)	-290(29.5)	268	0.203
Sandusky River									
26	-230(17.7)	-251(66.2)	+21(21.0)	-70(26.7)	-18(13.0)	+109(36.7)	-209(17.8)	224	0.140
28	-243(17.8)	-273(70.1)	+ 7(5.5)	-47(17.4)	-10(8.5)	+134(42.9)	-189(15.5)	257	0.191
44	-155(16.5)	-145(69.7)	-25(19.5)	+96(80.0)	- 4(6.9)	- 83(29.1)	-161(20.2)	159	0.221
45	-204(20.0)	-220(79.4)	-17(14.6)	+36(20.0)	-11(19.3)	- 99(33.5)	-311(33.6)	216	0.225
46	-240(22.7)	-220(77.5)	-12(9.8)	- 5(2.2)	- 7(12.7)	- 64(23.9)	-308(32.3)	219	0.226
47	-292(24.9)	-249(75.4)	- 8(5.9)	-62(22.3)	- 3(4.2)	+ 29(15.7)	-293(29.3)	258	0.201
49	-142(14.6)	-153(66.8)	+ 3(2.5)	+42(19.4)	- 1(2.3)	- 20(10.2)	-130(16.1)	209	0.192
51	-184(17.1)	-193(69.4)	+ 4(3.1)	+ 8(3.4)	- 4(8.3)	- 17(8.8)	-202(22.9)	247	0.200
52	-199(18.1)	-169(66.0)	-21(15.2)	+10(4.3)	- 1(2.2)	- 17(8.4)	-198(22.6)	227	0.221
Honey Creek									
32	-445(33.0)	-308(72.3)	-27(16.6)	-74(36.8)	- 8(10.5)	- 19(6.2)	-436(37.2)	298	0.224
33	-370(27.0)	-301(71.0)	-22(13.6)	-131(50.0)	-11(12.9)	- 3(0.9)	-468(37.8)	279	0.212
43	-262(24.8)	-222(68.9)	-23(18.1)	+71(46.7)	- 3(8.1)	- 58(22.0)	-235(26.1)	263	0.199
48	-201(20.3)	-168(66.1)	-26(18.1)	-18(9.1)	0	- 25(13.6)	-239(29.5)	211	0.223
Cuyahoga River									
29	-419(29.4)	-455(80.1)	0	+ 1(0.4)	-27(15.0)	+126(123.5)	-355(29.9)	422	0.189
Mean (All samples)	-261(22.0)	-233(70.8)	-10(6.9)	-19(4.6)	-10(9.0)	- 3(2.9)	-274(27.0)	246	0.205

* + indicates an increase during bioassays; - indicates a decrease. Values in parentheses represent the percent change in that chemical fraction during bioassays.

† Σ(ΔFractions) = (ΔR-NaOH-P) + (ΔNR-NaOH-P) + (ΔCDB-P) + (ΔHCl-P) + (ΔResidual-P).

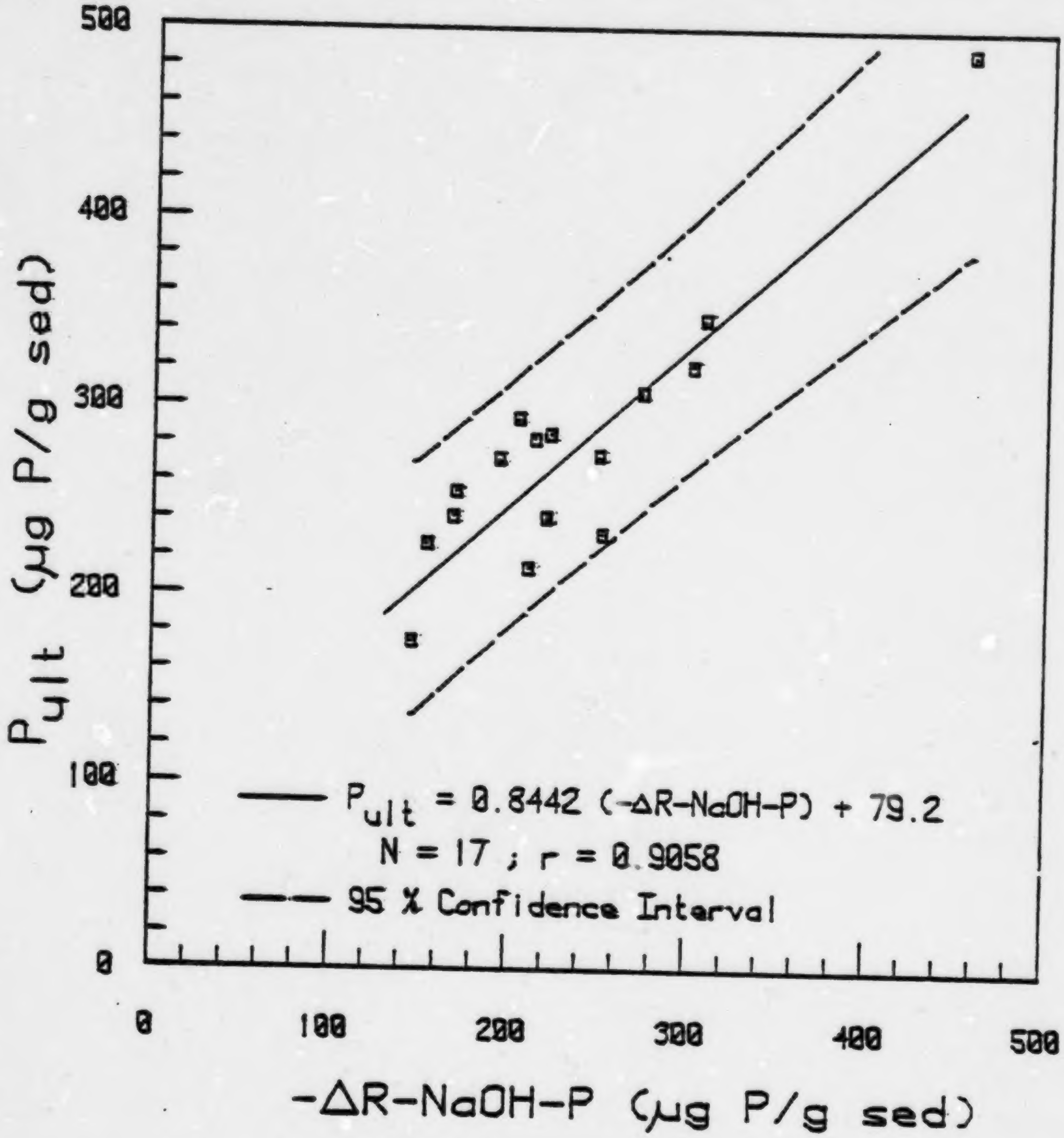


Figure 14. Regression line of P_{ult} versus the decrease in R-NaOH-P during bioassays (-ΔR-NaOH-P) superimposed on data for tributary suspended sediments.

fractions indicate that a rearrangement of sediment P forms may have occurred during bioassays on some samples. This is consistent with the results of Verhoff *et al*. (1978), who reported large increases in CDB-P during longer bioassays.

Other authors (e.g. Logan, *et al*, 1979; Allan and Williams, 1978) have suggested that all or part of the sediment P extractable by CDB reagents may be available for algal uptake. Based on the decreases in CDB-P observed during bioassays for several samples in this study, it appears that, in some cases, this fraction may make a significant contribution to algal-available P. However, this contribution tends to vary considerably, as indicated by the lack of correlation between P release in the DCDAs and ΔCDB-P ($r = 0.238$). In any event, the vast majority of bioavailable sediment P released during 3-4 week bioassays appears to originate from the R-NaOH-P fraction rather than the CDB-P fraction. Thus, the strong correlations noted earlier between R-NaOH-P and both P_{ult} and P_s may be attributed to a direct cause-effect relationship. The data provide no evidence of such a mechanistic relationship between CDB-P and sediment P bioavailability.

The overall first-order rate of available P release in the DCDAs (k_r in Table 11) was found to be closely correlated ($r = -0.6882$, $\alpha = 0.0023$) with the change in the Residual P fraction during the bioassays. This result is consistent with the significant correlation (Table 16) observed between k_r and Residual P measured before the bioassays. Release rate was even more strongly correlated ($r = -0.7975$, $\alpha = 0.0001$) with the change in the NR-NaOH-P fraction, although the relative magnitude of this change was small for all samples analyzed. It seems likely that the concentrations of Residual P and NR-NaOH-P were influenced by the level of microbial activity in the DCDAs. However, the proposal of a mechanism responsible for the observed correlations would require additional information on the fractionation of P associated with various microorganisms at different stages of growth and decomposition.

PARTICLE SIZE DISTRIBUTIONS AND SETTLING VELOCITY ANALYSES

Particle Size Distributions

Three types of plots were used to analyze the particle size distribution data obtained for tributary suspended sediments in this study. Plots of cumulative particle volume versus particle diameter were generated for all tributary samples, and the volume median particle diameter (D_{50v}) was determined from these as shown in Figure 15. For samples collected during the second year of the study, cumulative particle number was also plotted against

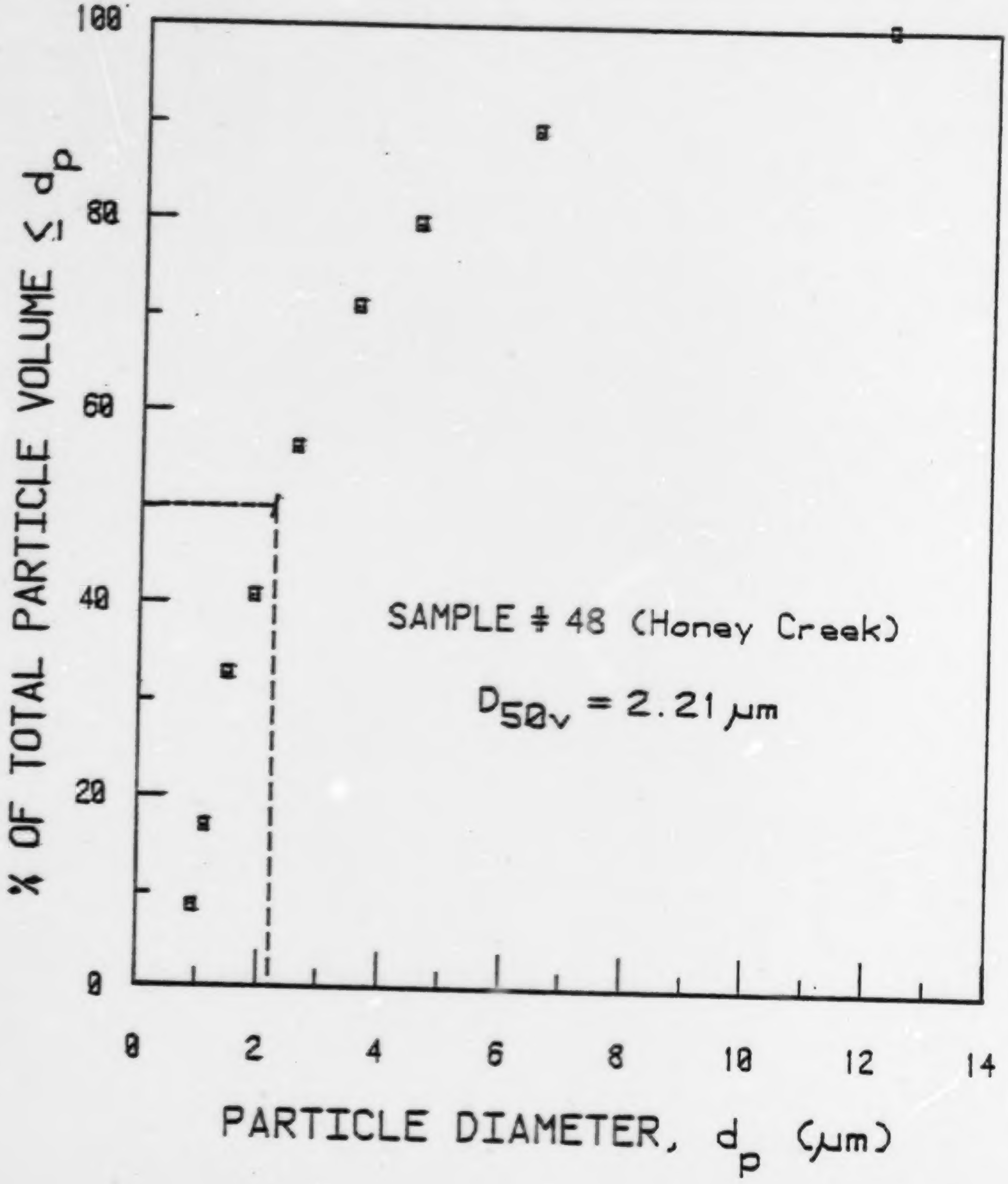


Figure 15. Cumulative particle volume versus particle diameter for Sample #48 (Honey Creek).

particle diameter (d_p) and the number median particle diameter (D_{50n}) obtained in a similar manner. In addition, plots of $\log(\Delta N/\Delta d_p)$ versus $\log d_p$ (see Equation 6) were used to calculate values of the power law exponent, β. An example of such a plot is presented in Figure 16. Separate estimates of β were obtained using counts made with 30 µm and 50 µm apertures (β_{30} and β_{50}, respectively) on the Coulter Counter. As seen in Figure 16, no particles were registered in some of the larger size ranges. These data points were eliminated from the linear regression analysis used to compute β.

The sediment particle size parameters for all tributary samples are listed in Table 22. Since the computer software used to produce the power law distribution plots had not yet been developed, β was not evaluated for samples #1-10. Also, the D_{50v} values for samples #1-10 are probably overestimated in Table 22 since counts were made with a 50 µm aperture only. An example of the discrepancy to be expected is shown in Figure 17. For sample #25, a volume median diameter of 2.70 µm was obtained using a 50 µm aperture only, while counts made with both 30 µm and 50 µm apertures yielded a D_{50v} of 2.40 µm.

The only particle size parameter available for comparison among all tributaries is the volume median particle diameter, D_{50v}. Based on these values, samples taken from the two New York rivers (Genesee and Cattaraugus) were found to contain larger suspended sediment particles than those from all of the Ohio rivers except the Cuyahoga. These results are consistent with information on surface soil texture in the Lake Erie basin, which indicates that, while the Cuyahoga River and Cattaraugus Creek drain almost exclusively silty loam soils, the Maumee River and Sandusky River watersheds contain extensive areas of finer, clay-sized soils (U.S. Army Corps of Engineers, 1982). The particle size data is also in agreement with the measurements of suspended solids <20 µm presented in Table 7, which also indicate that Cuyahoga River sediments were substantially larger than those from the other Ohio rivers. Coefficients of variation for D_{50v} values from individual tributaries ranged from 16.9% for the Cattaraugus Creek samples to 87.7% for the Cuyahoga River, while the C.V. among the mean D_{50v} values for all tributaries was 42.3%. All of the values obtained for the number median particle volume, D_{50n}, fell within the narrow range of 0.86 µm to 1.07 µm. The power law exponents also showed little variability, both

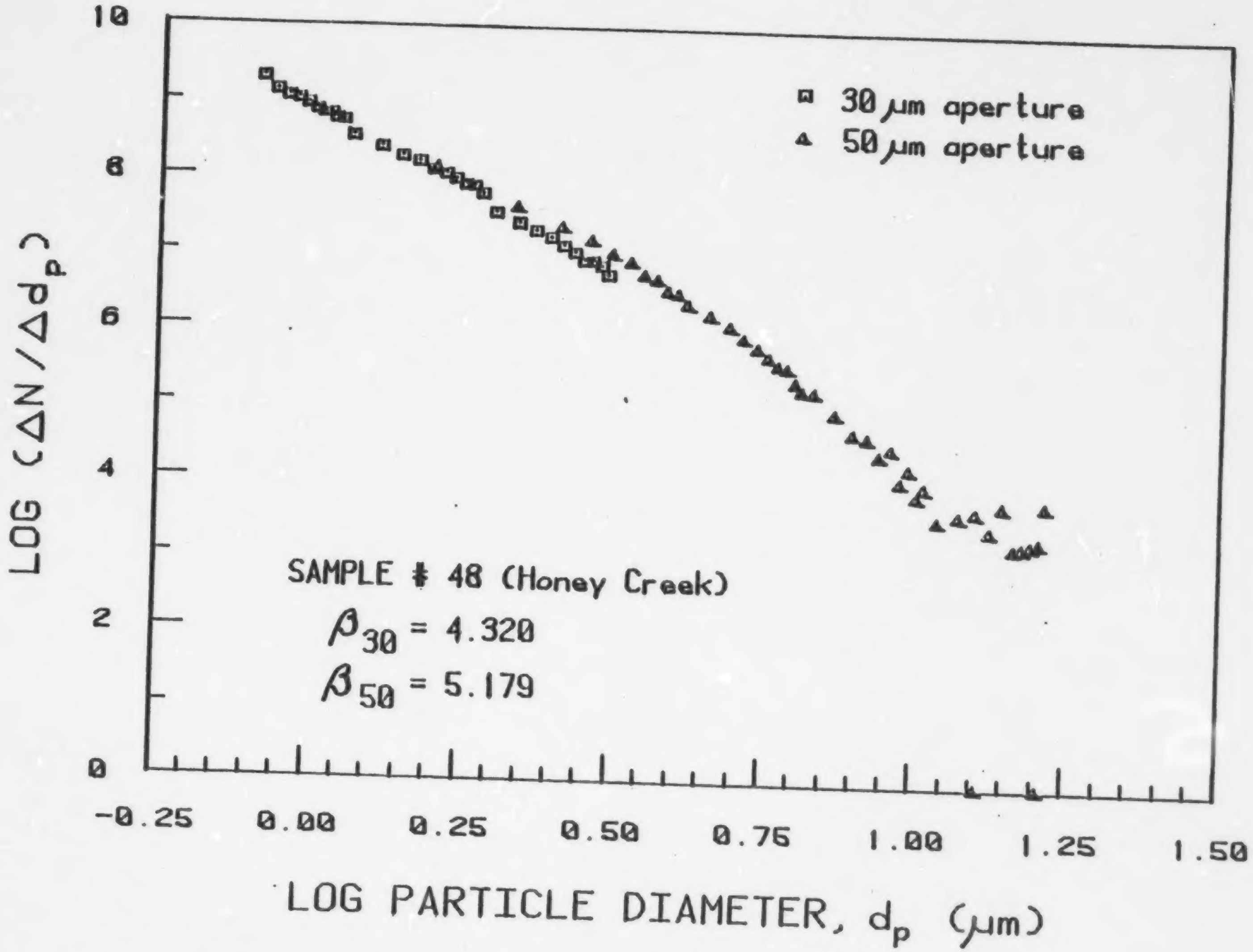


Figure 16. Power law distribution plot - log $(\Delta N/\Delta d_p)$ versus log d_p for Sample #48

TABLE 22. MEDIAN PARTICLE DIAMETERS AND POWER LAW EXPONENTS FOR TRIBUTARY SUSPENDED SEDIMENTS

Tributary	Sample #	Volume Median Particle Diameter	Number Median Particle Diameter	Power Law Exponent, β	
				30 μm	50 μm
Maumee River	5	3.15 μm	-	-	-
	8	2.73	-	-	-
	13	2.60	-	4.109	4.743
	15	2.30	-	4.250	4.433
	17	3.50	-	4.064	4.726
	19	2.55	-	4.302	5.782
	21	2.05	-	4.777	4.757
	27	6.16	0.87 μm	5.274	3.135
	41	3.60	1.06	4.105	5.102
	42	3.48	1.00	4.224	4.329
	50	1.30	0.90	5.520	4.297
	Mean	3.04	0.96	4.514	4.589
Sandusky River	2	2.95	-	-	-
	7	3.00	-	-	-
	11	1.70	-	5.018	4.795
	16	2.60	-	4.067	4.397
	20	1.70	-	4.311	5.830
	24	3.50	-	3.838	4.239
	25	2.40	-	4.342	5.048
	26	2.95	0.98	4.309	4.878
	28	2.85	1.03	4.071	4.728
	30	2.90	0.86	4.326	3.937
	31	1.75	0.87	3.657	3.096
	34	3.97	0.95	3.630	3.886
	35	2.69	0.91	5.470	5.244
	36	2.08	0.87	4.074	4.985
	37	3.21	1.01	4.365	4.193
	38	4.25	1.03	4.261	4.640
	38A	3.22	0.87	3.864	4.174
	39	4.50	1.06	3.964	4.338

(continued)

TABLE 22 (continued)

Tributary	Sample #	Volume Median Particle Diameter	Number Median Particle Diameter	Power Law Exponent, β	
				30 µm	50 µm
Sandusky River (cont'd)	40	4.50 µm	1.05 µm	3.980	4.525
	44	1.41	1.02	4.503	5.051
	45	2.42	1.01	4.638	4.896
	46	3.39	1.00	4.840	4.046
	47	1.85	0.97	5.189	5.213
	49	4.70	1.05	4.208	5.150
	51	1.45	1.02	5.231	5.288
	52	1.84	1.00	5.307	5.128
	Mean	2.84	0.98	4.394	4.654
Cuyahoga River	1	5.65	–	–	–
	4	15.30	–	–	–
	12	2.90	–	4.013	4.618
	29	2.95	0.87	5.280	4.935
	Mean	6.70	0.87	4.646	4.776
Genesee River	3	5.60	–	–	–
Cattaraugus Creek	6	4.65	–	–	–
	9	6.10	–	–	–
	10	6.50	–	–	–
	Mean	5.75	–	–	–
Honey Creek	32	2.78	0.96	4.908	4.819
	33	2.76	0.96	4.703	5.095
	43	1.56	0.99	5.231	5.650
	48	2.21	1.07	4.320	5.179
	Mean	2.33	0.99	4.790	5.186

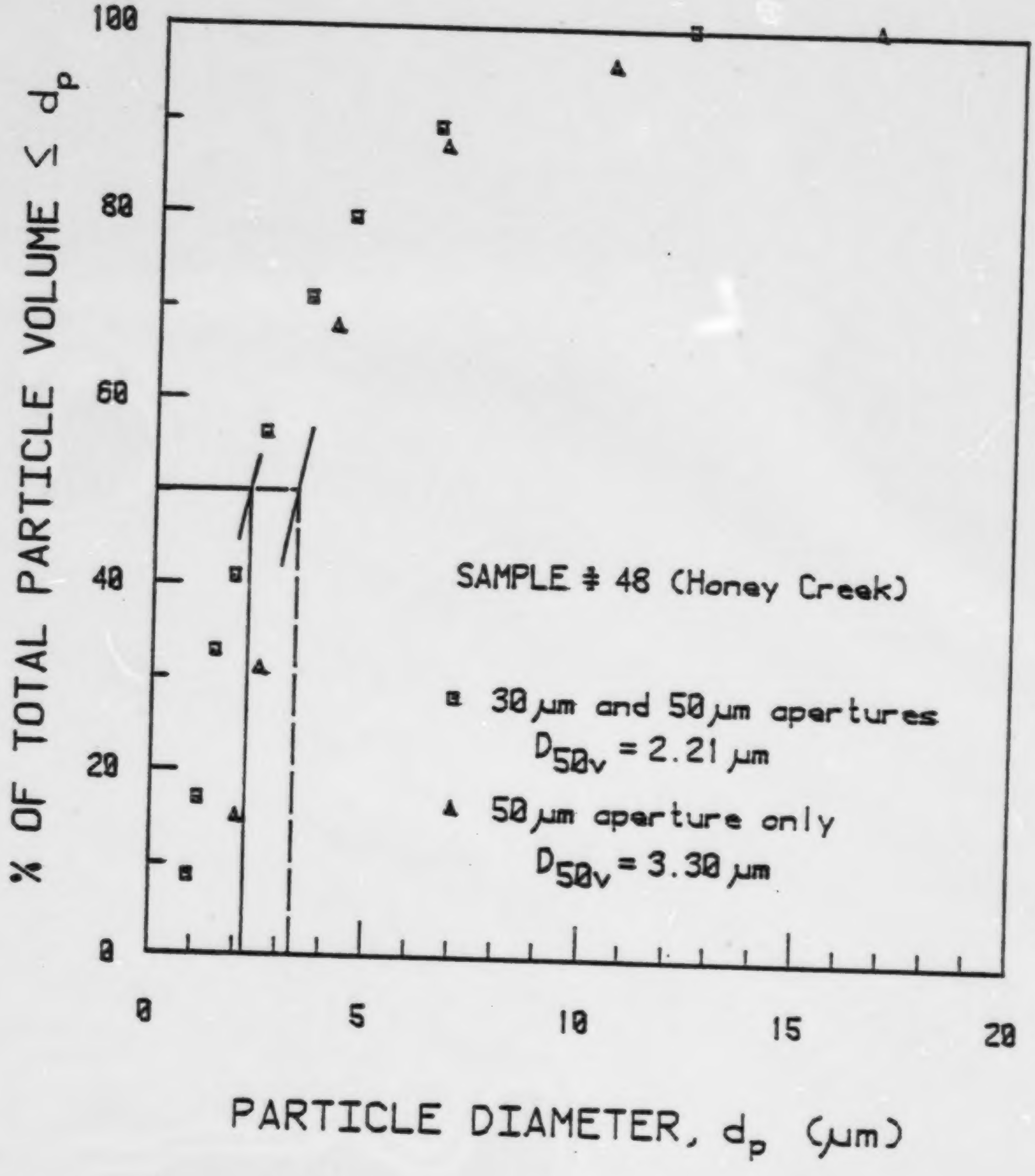


Figure 17. Comparison of cumulative volume distributions for Sample #48 (Sandusky R.) with and without 30μm aperature data.

among samples for a given tributary and between tributaries, although no figures were available for samples from the New York rivers. β_{30} and β_{50} both averaged over 4.0 for all of the Ohio tributaries. Thus, total particle number and surface area were predominately associated with smaller particle diameters, while particle volume was more evenly distributed among all size ranges. However, even the distribution of particle volume was skewed somewhat toward the smaller particle diameters. Despite substantial disagreement between β_{30} and β_{50} for some individual samples (e.g. sample #27), the mean values calculated for each tributary differed by less than 10%. In all cases, the mean β_{50} was slightly greater than the mean β_{30}.

In previous studies, Baker (1982a) found that sediment phosphorus concentrations (PP/SS) decreased as tributary suspended solids concentrations increased, while Armstrong et al. (1979) reported an inverse relationship between total sediment P (in ugP/g sediment) and sediment particle size. Based on these results, one might expect to find a shift toward higher percentages of large particles during periods of high flow. However, analyses conducted by Armstrong, et al. (1979) indicated that particle size distributions remained relatively uniform over wide ranges of total suspended solids concentration and flow for a particular tributary. Since Coulter counts were performed on 26 samples from the Sandusky River in the present study, it was possible to investigate correlations between the particle size parameters in Table 22 and other variables such as flow, total suspended solids concentration (TSS), T-Sed-P, P_{ult} and release rate (k_r). The simple correlation coefficients obtained from analysis of Sandusky River samples are listed in Table 23.

Based on the samples collected in this study, TSS in the Sandusky River was directly related to flow. Also, as reported by Baker (1982a), T-Sed-P showed a strong negative correlation with TSS. However, trends in sediment particle size are more difficult to interpret. Volume medium particle diameter, D_{50v}, was not significantly correlated with any of the parameters in Table 23. On the other hand, the number median diameter, D_{50n}, displayed significant inverse correlations with T-Sed-P and ultimately bioavailable sediment P (P_{ult}), as well as a direct relationship with flow. It is likely that these correlations were inflated somewhat by the narrowness of the range of D_{50n} values, in conjunction with wider variations in the other

TABLE 23. SIMPLE CORRELATION COEFFICIENTS BETWEEN SEDIMENT PARTICLE SIZE PARAMETERS AND VARIABLES RELATED TO THE FLUX AND BIOAVAILABILITY OF SEDIMENT P FOR SANDUSKY RIVER SAMPLES

		Flow	T-Sed-P	Total SS	P_{ult}	k_r
D_{50v}	r =	-0.1469	0.2451	-0.1337	0.1102	-0.0159
	α =	0.4739	0.2376	0.5149	0.6737	0.9517
D_{50n}		0.5330	-0.5439	0.4046	-0.7344	0.7149
		0.0188	0.0161	0.0857	0.0101	0.0134
β_{30}		0.4822	-0.3895	0.1936	0.2379	0.6766
		0.0170	0.0662	0.3646	0.3933	0.0056
β_{50}		0.5084	-0.6141	0.3936	-0.6148	0.4411
		0.0112	0.0019	0.0570	0.0147	0.0998
Flow		1.0000	-0.5511	0.7042	-0.1086	0.5189
		0.0000	0.0043	0.0001	0.6782	0.0328
T-Sed-P			1.0000	-0.7196	0.6124	-0.5008
			0.0000	0.0001	0.0090	0.0406
Total SS				1.0000	-0.3885	0.4386
				0.0000	0.1233	0.0782
P_{ult}					1.0000	-0.0863
					0.0000	0.7418

parameters. An example of this effect is given in Figure 18, which is a plot of D_{50n} versus flow, and is indicated by a nearly horizontal regression line. Nevertheless, since particle number and surface area are predominately associated with smaller diameter particles, it is reasonable to expect that D_{50n} would be more closely related than D_{50v} to the bioavailability parameters, P_{ult} and k_r. Both of the power law exponents, β_{30} and β_{50}, were also well correlated with flow. However, the correlation coefficients were positive, characteristic of a shift toward smaller particle sizes with increasing flows, rather than negative as would be expected. Similar results were found for the correlations between β_{50} and both T-Sed-P and P_{ult}, where the relationships were apparently close, but the signs of the correlation coefficients were again opposite to what was expected. Fluctuations in β_{30} and β_{50} values for the Sandusky River samples were small. Coefficients of variation for these two parameters were only 12.0% and 12.8%, respectively. Therefore, correlation coefficients involving the power law exponents may also have been enhanced by the relative uniformity of these values.

Correlation analyses based on all Sandusky River samples revealed no consistent relationships between sediment particle size and flow, T-Sed-P, TSS, or sediment P bioavailability. The possibility of such relationships was investigated further by comparing trends in these parameters over the course of individual storm runoff events. Volume median particle diameter (D_{50v}) and the power law exponent, β_{30}, have been plotted against sampling date along with flow and T-Sed-P for four 1981 runoff events on the Sandusky River (Figure 19). Evidence of the expected negative correlation between β_{30} and flow was seen for the first five samples taken during the June 9-16, 1981 period. The correlation coefficient for these parameters was $r = -0.9677$, although addition of data from the last two samples (June 15 and 16) lowered this considerably (to $r = -0.2363$). D_{50v} did not show a consistent trend as a function of flow for this event, but did for the period of May 14-17, 1981.

Based on Figure 19, it appears that over the course of some individual storm runoff hydrographs, as flow increases, sediment particle size may also increase while sediment P levels decrease. However, these relationships are generally not the same from one event to the next. For example, flows in the Sandusky River during the period of June 9-16 were considerably

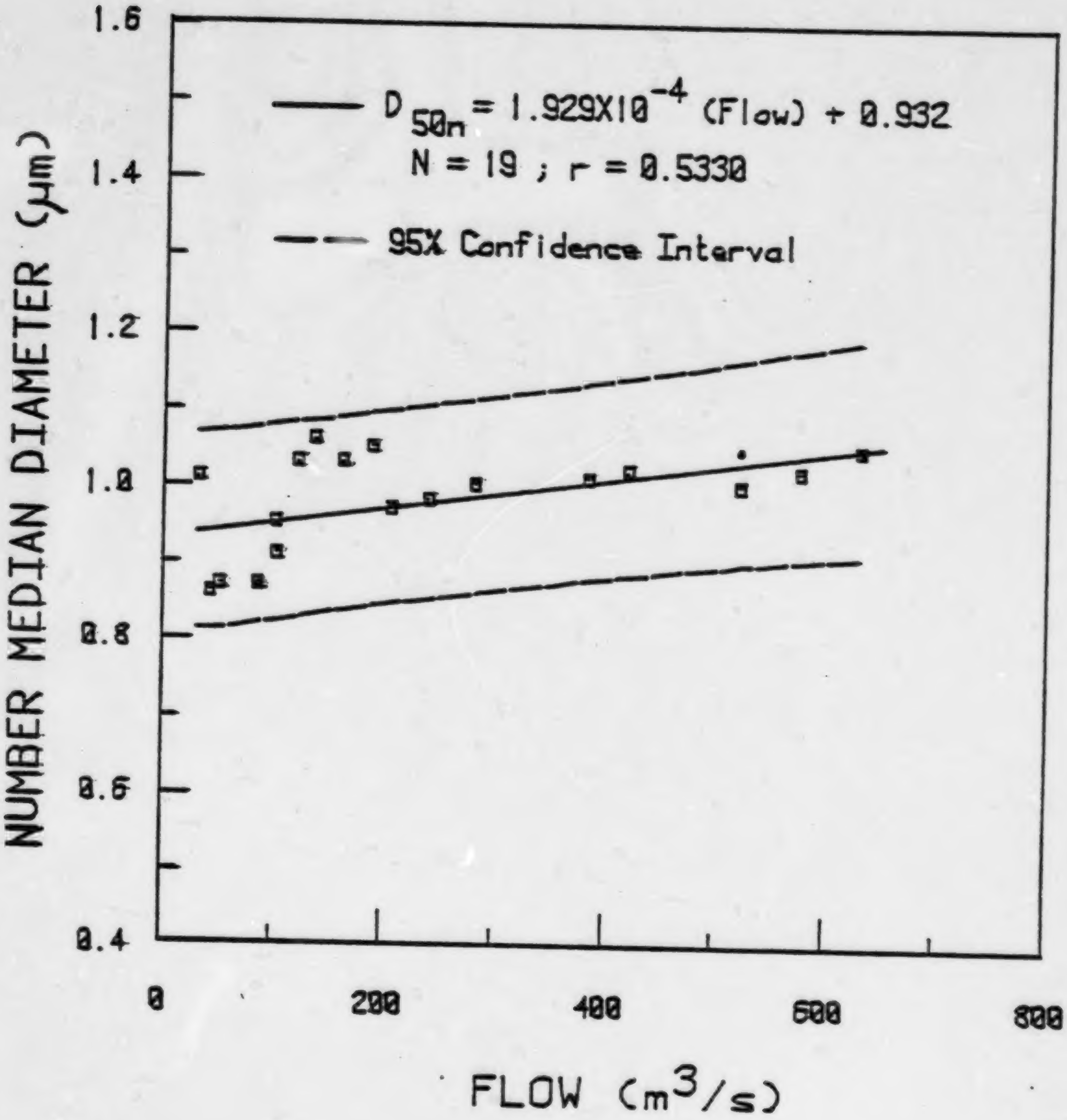


Figure 18. Regression line of D_{50n} versus flow superimposed on data for Sandusky River suspended sediments.

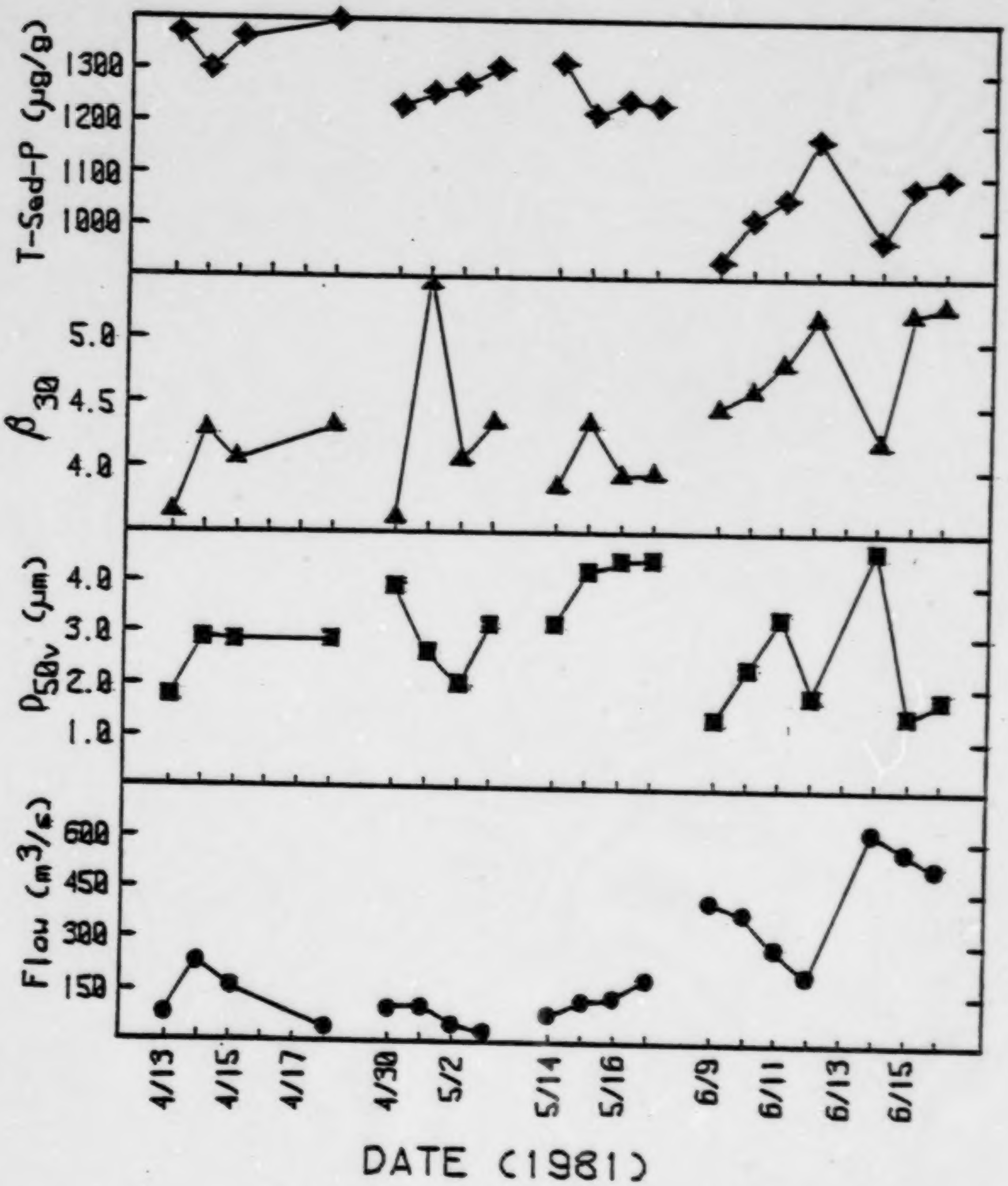


Figure 19. Comparison of trends in D_{50v}, β_{30} and T-Sed-P with flow over the course of four runoff events on the Sandusky River.

higher than for the three other storms monitored, and, as expected, T-Sed-P concentrations were lower. Ultimately bioavailable sediment P, P_{ult}, displayed trends similar to T-Sed-P, and was also lower for the June samples. But, β_{30} values measured for this event were noticeably higher, indicating a higher proportion of fine-grained particles compared to the earlier storms. Thus, other factors appear to exert a greater effect than particle size on the total and bioavailable P content of suspended tributary sediments. These might include the residence time of sediments in the tributary system and the SRP concentrations to which they are exposed during this period. In addition, the distribution of particle sizes for suspended sediments in a tributary is influenced by other factors besides flow. The relative amounts of rainfall transported to the river by surface flow and "interflow" can also be important, as well as the quantities and sizes of bottom sediments available for resuspension during high flows. Both of these factors depend upon the recent history of precipitation patterns in the river basin. With respect to the 1981 Sandusky River samples, it is possible that, during the low flows characteristic of the winter months, smaller sediment particles were resuspended from the river bottom and transported downstream, while coarse-sized particles remained intact. Then, the first high flow events in the spring capable of resuspending these larger sediments would tend to exhibit a greater proportion of coarse-grained particles than events later in the year. This could account for the lower β_{30} values obtained for high runoff periods in April and May of 1981. Also, the prolonged exposure of bottom sediments to the overlying river water during winter low flow conditions may have allowed an accumulation of phosphorus (by adsorption), resulting in higher levels of T-Sed-P and P_{ult} for the early spring events.

Settling Velocities

The median particle settling velocities measured for 28 of the tributary samples are listed in Table 24 (from Kwolek, 1982). These values were first calculated from the time required for a reduction in absorbance (at 750 nm) to 50% of the initial reading, and are denoted by the symbol SV_{50}. However, a given mass of coarse-grained particles in suspension will block less of the incident light than the same mass of finer sediments. Thus, a 50% decrease in absorbance corresponds to a larger decrease in suspended solids concentration (SS). The relationship between absorbance and SS was investigated for sample #44 by monitoring these two parameters at a fixed height in a large (8.6 cm diameter x 145 cm height) settling column. The results, shown in Figure 20, indicate that a decrease of 50% in the mass of

TABLE 24. MEDIAN PARTICLE SETTLING VELOCITIES FOR TRIBUTARY SUSPENDED SEDIMENTS

			Median particle settling velocity		
Tributary	Sample number	Sampling date	Based on 50% abs. decrease (m/day)	Based on 20% abs. decrease (m/day)	Calculated from D_{50v} and Stoke's Law (m/day)
Maumee River	27	4/14/81	1.36	4.54	2.66
	41	5/5/81	0.24	0.90	0.91
	42	5/11/81	0.30	0.93	0.85
	50	6/16/81	0.16	0.60	0.12
	Mean		0.51	1.74	1.13
Sandusky River	26	4/14/81	0.17	0.64	0.61
	28	4/15/81	0.22	0.92	0.57
	30	4/18/81	0.43	1.15	0.59
	31	4/13/81	0.40	1.47	0.21
	34	4/30/81	0.25	1.00	1.11
	35	5/1/81	0.25	1.25	0.51
	36	5/2/81	0.18	0.83	0.30
	37	5/3/81	0.26	0.81	0.72
	38	5/15/81	0.63	2.22	1.27
	38A	5/14/81	0.34	1.11	0.73
	39	5/16/81	0.22	0.83	1.42
	40	5/17/81	0.31	1.35	1.42
	44	6/9/81	0.15	0.51	0.14
	45	6/10/81	0.10	0.44	0.41
	46	6/11/81	0.10	0.39	0.81
	47	6/12/81	0.13	0.50	0.24
	49	6/14/81	0.23	0.88	1.55
	51	6/15/81	0.18	0.53	0.15
	52	6/16/81	0.14	0.47	0.24
	Mean		0.25	0.91	0.68

(continued)

TABLE 24 (continued)

Tributary	Sample number	Sampling date	Median particle settling velocity Based on 50% abs. decrease (m/day)	Median particle settling velocity Based on 20% abs. decrease (m/day)	Median particle settling velocity Calculated from D_{50v} and Stoke's Law (m/day)
Cuyahoga River	29	4/15/81	0.60	3.15	0.61
Honey Creek	32	4/14/81	0.17	0.68	0.54
	33	4/30/81	0.21	1.03	0.53
	43	5/10/81	0.08	0.31	0.17
	48	6/14/81	0.14	0.54	0.34
	Mean		0.15	0.64	0.39

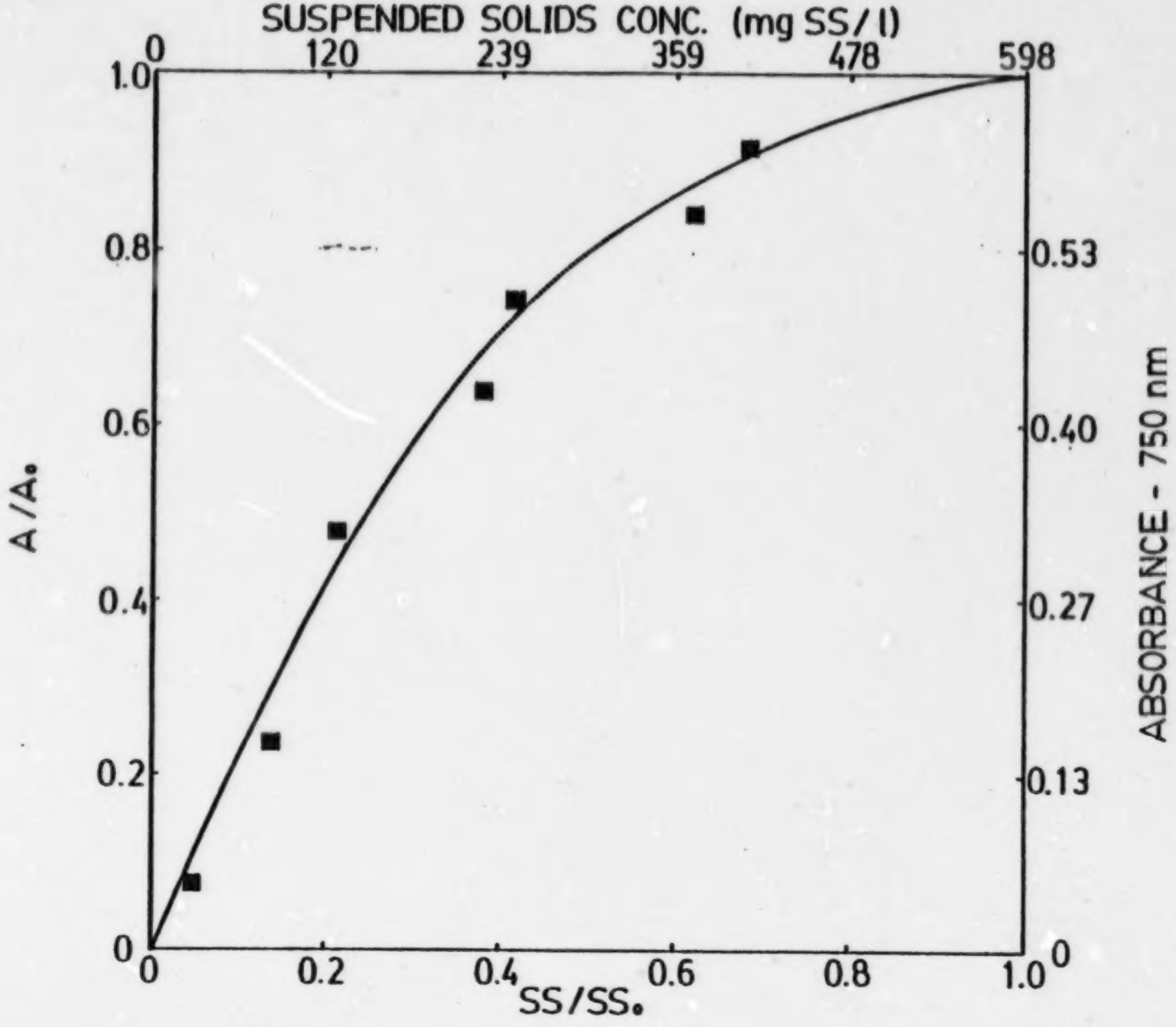


Figure 20. Relationship between normalized absorbance and normalized suspended solids concentration for sediments from Sample #44 (Sandusky River), based on a settling column analysis.

suspended solids at the sampling port resulted in only about a 20% decrease in absorbance. Although this percentage may vary somewhat from sample to sample, for the purpose of this study, it was assumed to be typical of all samples and a second series of median settling velocities was calculated based on the time required for a 20% decrease in absorbance (denoted by SV_{20}). In addition, another estimate of median particle settling velocity was obtained from the measured volume median particle diameter (D_{50v}) by applying Stoke's Law. For this calculation, it was assumed that the sediment particles had a density of 2.5 g/cm^3 and settled in water at 20 °C. Both SV_{20} and the Stoke's velocity are also listed in Table 24.

The median velocities based on a 20% decrease in absorbance were generally about 3.5 to 4 times as large as those based on a 50% decrease. For the majority of samples, the settling velocity calculated from D_{50v} using Stoke's Law fell between SV_{50} and SV_{20}.

An important application of settling velocity measurements is in predicting the residence time of tributary suspended sediments in the water column of the receiving water to which they are discharged. In the numerical example presented previously, a median residence period of 10 days was used in comparing model predictions of sediment P release in the western basin of Lake Erie (mean depth = 7.3 m). Although the median settling velocities obtained in this study were quite variable, 0.73 m/day would be a typical value, indicating that a 10 day residence time is a reasonable basis for model comparison.

Simple correlation coefficients between these median settling velocities and the sediment particle size parameters were calculated using the data from all samples, and are listed in Table 25A. As anticipated, particle settling velocity showed a fairly strong positive correlation with D_{50v} and a significant negative correlation to β_{50}. SV_{50} exhibited slightly stronger correlations with these two parameters than did SV_{20}. However, the implications of this result are uncertain, since the two settling velocities were found to be very closely related to one another ($r = 0.9634$). The correlations between the Stoke's Law settling velocity calculated from D_{50v} and the velocities measured by Kwolek (1982) were highly significant. Nevertheless,

TABLE 25. SIMPLE CORRELATION COEFFICIENTS INVOLVING MEDIAN PARTICLE SETTLING VELOCITIES

A) Correlations with Particle Size Parameters - All Tributary Samples

	Median Settling Velocity	
Parameter	SV_{50}	SV_{20}
D_{50v}	r = 0.6332 α = 0.0003	0.6010 0.0007
Stoke's Law Settling Velocity	0.7205 0.0001	0.6696 0.0001
D_{50n}	-0.4137 0.0286	-0.4366 0.0202
β_{30}	0.0727 0.7131	0.1160 0.5565
β_{50}	-0.5732 0.0014	-0.4748 0.0107

B) Correlations with Sediment P Flux and Bioavailability Parameters - Sandusky River Samples Only

	Median Settling Velocity	
Parameter	SV_{50}	SV_{20}
Flow	r = -0.4691 α = 0.0427	-0.5010 0.0289
TSS	-0.3836 0.1050	-0.4094 0.0817
T-Sed-P	0.5031 0.0281	0.4911 0.0327
P_{ult}	0.7957 0.0067	0.7380 0.0095
k_r	-0.7642 0.0062	-0.8492 0.0009

the agreement between these values was somewhat disappointing. The observed discrepancies were most likely due to the effects of dispersion in the spectrophotometer cell in which settling velocities were measured and to variations in the relationship between suspended solids concentration and absorbance from sample to sample. Neither D_{50n} nor β_{30} displayed the expected relationship with settling velocity.

Correlation coefficients between the median settling velocities and flow, T-Sed-P, TSS, P_{ult} and k_r for the Sandusky River samples were also determined. These values are presented in Table 25B. The results followed essentially the same trend as was found for correlations between these parameters and β_{50} (see Table 23). That is, although relationships appeared to exist with some of the parameters (flow, T-Sed-P, and P_{ult}), the correlation coefficients were opposite in sign to what was expected based on previous studies. One exception is the strong inverse correlation between settling velocity and the first-order release rate of bioavailable sediment P. Rapid settling velocities would typically be displayed by larger particles. Provided other factors, such as chemical composition and level of biological activity, were relatively constant, these larger particles should release sediment P more slowly than fine-grained particles since they have a smaller surface area (per unit weight of sediment) at which the release reaction(s) may occur. The significant positive correlation between β_{30} and k_r (Table 23) constitutes additional evidence that larger sediment particles released P more slowly in this study, at least for samples from the Sandusky River.

Trends in SV_{50} over the course of individual runoff events on the Sandusky River are shown in Figure 21, and compared with changes in flow, TSS, and k_r. These results are in agreement with those in Figure 19. Although samples from the June 9-16 runoff event were taken at higher flows and contained higher TSS concentrations than those from the earlier events, the suspended sediment particles in the June samples were generally smaller and settled more slowly. This is surely responsible for many of the unexpected correlation coefficients seen in Tables 23 and 25. It is possible that these correlations would change if data from a larger number of Sandusky River samples were included. However, the information presented here provides a strong indication that the relationship between sediment particle size and tributary flow may vary widely from one storm runoff event to the next, as may the relationship between sediment particle size and sediment phosphorus content.

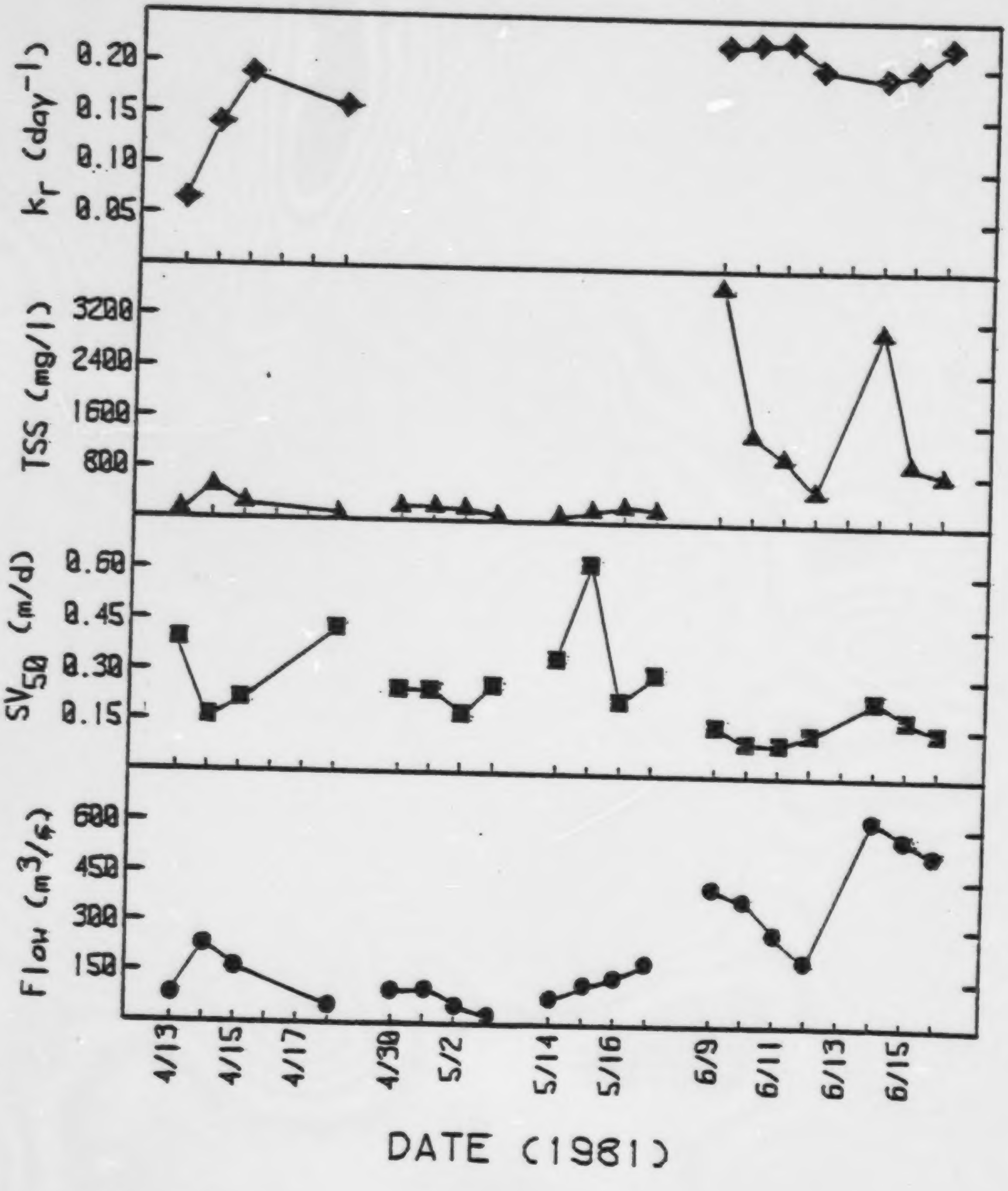


Figure 21. Comparison of trends in SV_{50}, TSS, and k_r with flow over the course of runoff events on the Sandusky River.

LAKE ERIE BLUFF AND BOTTOM SEDIMENT SAMPLES

The erosion of shoreline (bluff) sediments and the resuspension of lake bottom sediments during high wind periods both may result in substantial inputs of particulate P into the water column of Lake Erie (Sonzogni, et al., 1982; Lam and Jaquet, 1980). The biological availability of sediment P in samples from these sources was investigated using chemical fractionation and bioassay analyses. The results are presented in Table 26. These data are especially interesting since they encompass much wider extremes of sediment P fractionation and bioavailability than do the tributary data.

The eroding bluff material contained extremely low levels of NaOH- and CDB-extractable P. In addition, the T-Sed-P concentrations of the Port Stanley and Rondeau Park samples were well below the lowest value measured for tributary sediments. A large percentage (mean = 78.3%) of T-Sed-P in the bluff samples was removed in the HCl extraction step, and therefore, was most likely present in the form of apatite P. By comparison, although concentrations (in μgP/g sediment) were similar for Cattaraugus Creek sediments, HCl-P made up only 47.9% of T-Sed-P. In DCDA bioassays on these samples, none of the sediment P became available to algae during the course of the experiments. This is consistent with the assertion made by other researchers (e.g. Williams, et al., 1976; Logan, 1978; Young, et al., 1982) that apatite P is virtually unavailable to aquatic organisms. Previous studies conducted on recessional shoreline sediments have also indicated that they contain very low levels of bioavailable sediment P (Sonzogni, et al., 1982).

The Monroe bottom sediment samples represent the opposite extreme from the bluff sediments. Concentrations of T-Sed-P, T-NaOH-P, and CDB-P in the Monroe #2 sample were all more than twice as large as the highest values observed for tributary suspended sediments. Bioassays showed that P_{ult} for both Monroe samples was also over twice the largest value measured for tributary sediments. The percentage of T-Sed-P available to algae (over 50%) was greater as well. Bottom sediments from the Toledo sites, on the other hand, exhibited chemical fractionation and bioavailability characteristics well within the ranges measured for tributary suspended sediments.

Lake bottom sediments consist of a combination of allochthonous and autochthonous particulates which have, during and after deposition, undergone a variety of physical, chemical, and biological transformations. The results obtained for Toledo bottom sediments suggest that they are composed largely of allochthonous material. Much of this material probably originates from the Maumee River, which delivers large quantities of suspended sediments to Lake Erie at Toledo. In fact, the characteristics of the Toledo bottom sediments closely resemble

TABLE 26. CHEMICAL FRACTIONATION AND BIOASSAY RESULTS FOR SHORELINE EROSION (BLUFF) AND LAKE BOTTOM SEDIMENT SAMPLES

A) Chemical Fractionations (Values in μgP/g sed.):

Sample (Type)	T-Sed-P	T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
Monroe #1(bottom)	2266	1321	1226	95	475	258	44
Monroe #2(bottom)	3551	1863	1796	67	612	315	43
Toledo #1(bottom)	926	208	156	53	156	248	105
Toledo #2(bottom)	935	226	187	40	167	227	99
Port Stanley(bluff)	279	13	8	5	94	228	25
Rondeau Park(bluff)	396	8	6	2	22	326	28
L. Superior(bluff)	771	15	13	2	32	543	88

B) DCDA Bioassays (One-Component Release Coefficients Calculated by Thomas Method):

Sample	T-Sed-P in DCDA's (μgP/g sed.)	Sediment P Released in in DCDA's (μgP/g sed.)	Ultimately Bioavailable Sediment P, P_{ult}(μgP/g sed.)	P_{ult} as a % of T-Sed-P	Release Rate, k_r (day^{-1})
Monroe #1	2656	964.2	1435.0	54.0	0.042
Monroe #2	3044	1341.3	1482.4	48.7	0.080
Toledo #1	947	99.3	99.3	10.5	0.140
Port Stanley	662	0	0	0	–
Rondeau Park	557	0	0	0	–

those of Maumee River sediments from which 50-75% of the ultimately available sediment P has been released. P_{ult} for the Toledo #1 sample was measured at 99.3 μgP/g sediment, compared to a mean of 337.3 μgP/g sediment for Maumee River suspended sediments, while k_r was found to be very close to the mean slow component release rate (k_{sr}) for Maumee River samples (Table 13). In addition, the commonly employed chemical measures of available P (i.e. R-NaOH-P and NAIP) were substantially lower for the Toledo bottom sediments than for Maumee River suspended sediments.

As mentioned previously, the Monroe bottom sediments contained much higher levels of T-Sed-P than any of the tributary sediments analyzed. Based on the sampling location from which the Monroe bottom sediments were obtained, it is likely that the deposition of autochthonous particulate material, such as phytoplankton, is largely responsible for the observed enrichment in sediment P. This enrichment occurred almost exclusively in the R-NaOH-P pool, and to a lesser extent in the CDB-P fraction (see Table 26), or the non-apatite inorganic components of sediment P. Therefore, it must have taken place via a decomposition-mediated mineralization of autochthonous P at the lake bottom, followed by reentry into the bottom sediments through adsorption or precipitation.

The results of DCDA bioassays performed on Monroe bottom sediments also suggest the influence of autochthonous particulate material at this site. First-order release rates measured for these samples were less than the mean slow component release rate, k_{sr}, for suspended sediments from any of the tributaries (Table 13). Bottom sediments receiving a steady influx of phytoplankton biomass would no doubt develop a large decomposer population. It is possible that P released from the Monroe sediments in the DCDAs was immobilized temporarily by such bacteria. This P would be re-released upon subsequent decomposition of (or endogenous respiration by) these organisms, resulting in a slower measured release rate.

The data of Table 26 indicate that the chemical nature of P in Lake Erie bottom sediments may vary considerably as a function of location in the lake. The amount of available P released from bottom sediments during periods of resuspension will depend primarily on the point of origin within the lake and the duration of residence in the water column. Sediments receiving large influxes of autochthonous material may make substantial contributions of available P to the water column upon resuspension. For example, based on bioassay results, the Monroe bottom sediments would release as much sediment P during a 3 day resuspension period as would be released by Maumee River suspended sediments during a 7 day period.

SANDUSKY RIVER BOTTOM SEDIMENT SAMPLES

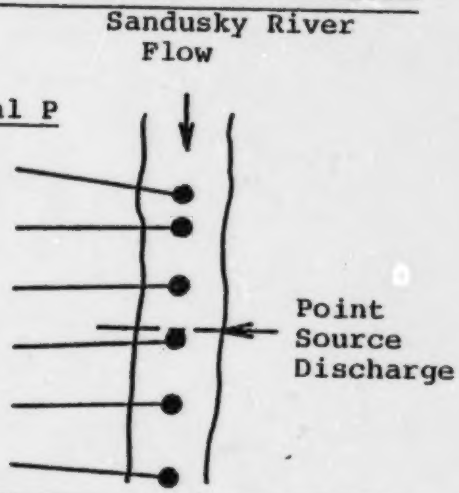
The effect of a point source of phosphorus on the sediment P chemistry was also briefly examined in this study. The chemical fractionation sequence was applied to bottom sediment samples from three sites upstream and three sites downstream from the Bucyrus, Ohio wastewater treatment plant discharge (on the Sandusky River). The results are given in Table 27. Substantial increases in the R-NaOH-P and CDB-P fractions occurred downstream of the point source. The NR-NaOH-P, HCl-P, and Residual P fractions were also found to increase, but by smaller amounts. This movement of phosphorus into the sediments is consistent with the finding by Baker (1982a) that soluble reactive P concentrations decreased rapidly with distance downstream from the Bucyrus treatment plant discharge. However, Baker (1982b) has suggested that P from such point sources is not exported as R-NaOH-P, and thus, does not contribute significantly to the input of bioavailable particulate phosphorus to the receiving water. The data presented in Table 27 indicate that, although much of the point source P may be tied up in relatively unavailable forms such as CDB-P, HCl-P, and Residual P, a sizable amount is also present as R-NaOH-P, and is therefore potentially bioavailable.

It appears that phosphorus from the point source is capable of assuming a number of different chemical forms in association with sediments. Baker (1982b) suggested that biological processes were more important than physical adsorption in the processing of point source inputs. The increases in R-NaOH-P and CDB-P observed in the present study, however, indicate the activity of physicochemical mechanisms. Biological activity also appears to play a role, although a less important one, in the fixation of point source P, as suggested by the large increase in NR-NaOH-P for site #6. It should be noted that the work of Baker (1982b) was conducted on suspended sediments from the Sandusky River, rather than on bottom sediments. The processing of P inputs by the indigenous algal population would be a more important factor in the water column of the river than in the bottom sediments. However, the environment should also be favorable for an increase in the R-NaOH-P concentration of suspended sediments by adsorption of SRP from solution. CDB-P, on the other hand, would be more likely to accumulate in the bottom sediments than in suspended sediments, since higher levels of soluble species such as Fe^{+3} and Al^{+3} are typically found at the sediment-water interface. These may result in the formation of iron or aluminum oxide coatings on the surface of sediment particles, and thus, the occlusion of surface-bound phosphorus.

Although an indirect point source of phosphorus may cause a substantial increase in the amount of available P bound to

TABLE 27. EFFECTS OF A POINT SOURCE DISCHARGE ON PHOSPHORUS FRACTIONATION IN SANDUSKY RIVER BOTTOM SEDIMENTS

Site no.	Miles from point source	Concentrations in µgP/g sediment T-Sed-P	T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
1	9	777	284	215	69	214	125	107
2	7	644	226	177	49	160	123	91
3	3	470	55	43	12	92	263	54
4	0.5	1510	528	434	94	452	249	132
5	5	1039	397	320	77	308	165	119
6	10	1404	596	305	291	177	323	170


Sandusky River
Flow
Point
Source
Discharge

sediments, on the whole, attachment of this P to particulate material causes a decrease in its potential bioavailability. DePinto et al. (1980) performed bioassay measurements of phosphorus availability on effluents from four municipal sewage treatment plants in the Lower Great Lakes basin. They reported that an average of 72% of the total P - 55% of the particulate P fraction and 82% of the total soluble fraction - was available for uptake by *Scenedesmus* sp. Incorporation of this highly available phosphorus into the CDB-P, HCl-P, and Residual P fractions of the bottom sediments essentially immobilizes a portion of the point source P. Based on the data collected in this study, however, it is not possible to quantify the reduction in the bioavailability of P from the Bucyrus treatment plant due to processing in the river. This would require characterization of P associated with suspended particulates as well as soluble P concentrations as a function of distance downstream from the point source discharge.

SECTION 5

IMPLICATIONS OF RESULTS FOR PHOSPHORUS MANAGEMENT

As part of the effort to reduce the productivity of the Lower Great Lakes, target phosphorus loads were established by Task Group III (1978). These were based on total P and were set at 11,000 metric tons/year for Lake Erie and 7,000 metric tons/year for Lake Ontario. However, the results of this study indicate that the various forms of P present in inputs to these lakes often have vastly different degrees of availability to aquatic organisms. For example, sediment P associated with Lake Erie bluff material was totally unavailable to *Selenastrum*, while SRP inputs from the Ohio tributaries were nearly all rapidly available. In the existing phosphorus budgets for the Lower Great Lakes, inputs are broken down into two forms - soluble and particulate. Such budgets may not provide an entirely accurate picture of the relative contribution of each source to productivity in the receiving water. An improvement could be made by separating the particulate P inputs into ultimately available and unavailable fractions. Based on the results of the present study, Salisbury *et al*. (1983) have made preliminary revisions of loading estimates by the U.S. Army Corps of Engineers for Lake Erie to reflect the bioavailability of PP. Expressing target loads for the Lower Great Lakes in terms of the sum of bioavailable fractions should result in a clearer idea of the steps necessary to achieve the desired improvements in water quality. In this way, a more efficient appropriation of resources for upgrading the trophic condition of these lakes might be realized.

The existing target total P loads were developed through the application of mathematical models of lake trophic status. If external loads are separated into three different forms - SRP, ultimately available PP, and refractory PP - as suggested above, certain changes in the structure of these models would be necessary. The concept of differing bioavailability of P sources is already built into the current Great Lakes models to a certain extent. For example, phytoplankton in the water column are assumed to utilize only phosphorus present as SRP. Also, forms of sediment P having an extremely low degree of bioavailability, such as inputs from Lake Erie bluff erosion, are often eliminated from the loading data. Particulate P in the water column is assumed to be released to solution (as SRP) at a fixed first-order rate.

In the existing models, all P associated with suspended particulate material is considered to be capable of conversion to SRP. The rate at which this conversion takes place is assumed to be the same for all forms of PP regardless of its origin. However, the results of this study indicate that a sizable fraction of PP in tributary suspended sediments is unavailable for algal uptake. The percentage available varies among tributaries with differences in soil and land use conditions. In addition, it appears that allochthonous particulate material exhibits much different P release kinetics than autochthonous material in the water column. Sediment inputs from tributary sources generally release PP at a faster first-order rate, but less completely than decomposing algal biomass. Lake bottom sediments, which contain both types of material, exhibit bioavailability characteristics that are influenced by both components. Modification of the existing models to account for the different bioavailability kinetics of allochthonous and autochthonous particulate P would result in a more realistic mechanistic description of in-lake processes. This, in turn, would tend to minimize any artificial adjustments in the model coefficients that may be necessary to calibrate the existing models. With this change, the models should also provide more accurate predictions of the response of lake water quality to reductions in the phosphorus loads from various sources. Preliminary work conducted by Salisbury et al. (1983) using the model developed by DiToro and Matystik (1980) for Lake Erie has indicated that implementation of the changes mentioned above is feasible.

Lake bottom sediments are composed of a combination of allochthonous and autochthonous particulate material. The results obtained in this study suggest that, where influxes of the latter are relatively large, the bottom sediments may undergo a significant enrichment in sediment P. Also, much of this may be present in biologically available forms. Therefore, the resuspension of bottom sediments during high wind periods in the shallower basins of Lake Erie represents a potentially important source of available P. The Great Lakes models currently employed, in general, do not include a term to account directly for the input of P via resuspension of bottom sediments. This phenomenon may be partially accounted for by adjustment of particulate settling velocities to effect a calibration for particulate P concentrations in the water column. However, inclusion of an expression describing sediment resuspension, in combination with the availability kinetics of the associated P, should result in an improvement in the model predictions.

Differentiation between allochthonous and autochthonous sources of particulate P in Great Lakes water quality models requires that the bioavailability of sediment P inputs be characterized. This may be accomplished most accurately using bioassay measurements such as the DCDA technique employed in this study. Since these methods tend to be quite time-consuming, however, chemical extractions are often used to estimate the bioavailability of sediment P. In this study, P released during the bioassays on tributary suspended sediments was found to be associated predominately with the R-NaOH-P fraction. Other chemical fractions (such as CDB-P and T-Sed-P) were also strongly correlated with P_{ult}. However, it is felt that predictions of P_{ult} should be based on either R-NaOH-P or NAIP (= R-NaOH-P + CDB-P), since the data indicate a mechanistic as well as a statistical connection between R-NaOH-P and bioavailability. None of the chemical fractions measured in this study provided accurate predictions of the first-order sediment P release rate, k_r. Release rate did not exhibit much fluctuation either among samples for a given tributary or between tributaries.

Based on bioassays and extractions conducted during the first year of this study, Salisbury _et al_. (1983) considered the following percentages of particulate P inputs to be ultimately available for algal uptake in the water column of Lake Erie:

1) Detroit River - 20% (from regression of P_{ult} versus R-NaOH-P);
2) Western Basin (excluding Detroit R.) - 25% (from bioassays on Maumee R. samples);
3) Central Basin - 28% (from bioassays on Sandusky R. and Cuyahoga R. samples);
4) Eastern Basin - 8% (from bioassays on Cattaraugus Cr. samples).

These authors assumed the rate of sediment P release to be the same for all sources - 0.154 day^{-1}, based on the average of all bioassay measurements. When the bioassay results from the second year of this study were added to the data set, the same averages were obtained for the percentages of T-Sed-P available from tributary sources in all basins. However, the average release rate for all Lake Erie tributary samples from both years was found to be 0.180 day^{-1}. The bioavailability kinetics for P associated with Lake Erie bottom sediments were found to vary considerably as a function of location in the lake.

The information on bioavailability of sediment P inputs gathered in this study can serve as a preliminary basis for implementing the changes in phosphorus loading calculations and model structure suggested above. However, this should be supplemented with additional data from the tributaries studied and others in the Lower Great Lakes basin, as well as for bottom sediments at locations where resuspension is likely. Characterization of Detroit River suspended sediments is especially important, since this source constitutes over 40% of the total PP input to Lake Erie.

An analytical program combining the accuracy of bioassay measurements with the efficiency of chemical fractionation studies has been shown to be an effective means of quantifying sediment P bioavailability. The results presented in this report indicate that bioavailability remains relatively constant for a given set of soil type (i.e. geochemistry and texture) and land use conditions. Evidence of this is seen in the similarity between the bioassay and fractionation results for the Maumee and Sandusky Rivers. Also, Cattaraugus Creek sediments, which were much higher in apatite content, showed a distinctly lower level of P availability. The Cuyahoga River, which experiences a greater anthropogenic influence, displayed a higher level of sediment P bioavailability. Relatively little fluctuation in sediment characteristics was observed over time for any given tributary. Based on these findings, it is felt that future monitoring programs should concentrate on identifying differences between regions of distinct soil type and land use. This can be accomplished most readily using routine chemical extraction analyses on sediments transported during storm runoff events supplemented by less frequent bioassay measurements of sediment P bioavailability.

REFERENCES

Allan, R.J., and J.D.H. Williams, "Trophic Status Related to Sediment Chemistry of Canadian Prairie Lakes." J. Environ. Qual., 7, 99-106 (1978).

APHA, AWWA, and WPCF, Standard Methods for the Examination of Water and Wastewater, 14th Edition, Washington, DC (1976).

Armstrong, D.E., R.F.Harris, and J.K. Syers, "Plant Available Phosphorus Status of Lakes." Final Technical Completion Report, OWRR B-022-WIS, 29 pp. (1971).

Armstrong, D.E., J.J. Perry, and D.E. Flatness, "Availability of Pollutants Associated with Suspended or Settled River Sediments Which Gain Access to the Great Lakes." USEPA Technical Report No. 905/4-79-028, Region V, Chicago, Illinois (1979).

Atkinson, R.J., A.M. Posner, and J.P. Quirk, "Kinetics of Isotopic Exchange of Phosphate at the α-FeOOH-Aqueous Solution Interface." J. Inorg. Nucl. Chem., 34, 2201-2211 (1972).

Autenrieth, R.L., "The Effects of Acid Lake Recovery by Chemical Manipulation on Algal Growth Potential." M.S. Thesis, Clarkson College of Technology, Potsdam, NY (1981).

Bache, B.W., "Aluminum and Iron Phosphate Studies Relating to Soils: I. Solution and Hydrolysis of Variscite and Strengite." J. Soil Sci., 14, 113-123 (1963).

Bache, B.W., "Aluminum and Iron Phosphate Studies Relating to Soils: II. Reactions Between Phosphate and Hydrous Oxides." J. Soil Sci., 15, 110-116 (1964).

Baker, D.B., "Upstream Point Source Phosphorus Inputs and Effects." Seminar on Water Quality Management Tradeoffs: Point Source vs. Diffuse Source Pollution, Chicago, Illinois, EPA-905/9-80-009, 227-239 (1980).

Baker, D.B., "Fluvial Transport and Processing of Sediments and Nutrients in Large Agricultural River Basins." LEWMS Technical Report, U.S. Army Corps of Engineers, Buffalo, N.Y. (1982a).

Baker, D.B., "Characteristics of the Transport of Bioavailable Particulate Phosphorus in the Sandusky River Basin." Final Report to Proctor and Gamble Co., Cincinnati, Ohio (1982b).

Barrow, N.J., "The Description of Desorption of Phosphate from Soil." J. Soil Sci., 30, 259-270 (1979).

Bauwin, G.R., and E.H. Tyner, "The Nature of Reductant-Soluble Phosphorus in Soils and Soil Concretions." Soil Sci. Soc. Am. Proc., 21, 250-257 (1957).

Beckwith, W.R., "Chemical Fractionation as an Indicator of Phosphorus Bioavailability in Suspended Solids from Tributaries to Lake Erie." Master's Thesis, Clarkson College of Technology, Potsdam, NY (1982).

Bierman, V.J., Jr., D.M. Dolan, E.F. Stoermer, J.E. Gannon, and V.E. Smith, "The Development and Calibration of a Spatially Simplified Multi-Class Phytoplankton Model for Saginaw Bay, Lake Huron." Great Lakes Environmental Planning Study (GLEPS), Contribution No. 33, Great Lakes Basin Commission (1980).

Bonner, J.S., J.V. DePinto, and P.W. Rodgers, "Analysis of Aquatic Particle Size Distributions Using a Computer-Interfaced Coulter Counter." Clarkson College of Technology, In preparation (1983).

Bray, R.H., and L.T. Kurtz, "Determination of Total, Organic, and Available Forms of Phosphorus in Soils." Soil Sci., 59, 39-45 (1945).

Breeuwsma, A., and J. Lyklema, "Physical and Chemical Asorption of Ions in the Electrical Double Layer on Hematite (α-Fe_2O_3)." J. Colloid Interface Sci., 43, 437-448 (1973).

Burwell, R.E., D.R. Timmons, and R.F. Holt, "Nutrient Transport in Surface Runoff as Influenced by Soil Cover and Seasonal Periods." Soil Sci. Soc. Am. Proc., 39, 523-528 (1975).

Cahill, T.H., P. Imperato, and F.H. Verhoff, "Evaluation of Phosphorus Dynamics in a Watershed." J. Environ. Eng. Div., Proc. Am. Soc. Civ. Eng., 100, No. EE2, 439-458 (1974).

Carignan, R., and J. Kalff, "Quantification of the Sediment Phosphorus Available to Aquatic Macrophytes." J. Fish. Res. Bd. Can., 36, 1002-1005 (1979).

Chang, S.C., and M.L. Jackson, "Fractionation of Soil Phosphorus." Soil Sci., 84, 133-144 (1957).

Chapra, S.C., and W.C. Sonzogni, "Great Lakes Total Phosphorus Budget for the Mid-1970's." J. Water Pollut. Control Fed., 51, 2524-2533 (1979).

Chen, Y.R., J.N. Butler, and W. Stumm, "Adsorption of Phosphate on Alumina and Kaolinite from Dilute Aqueous Solutions." J. Colloid Interface Sci., 43, 421-436 (1973a).

Chen, Y.R., J.N. Butler, and W. Stumm, "Kinetic Study of Phosphate Reaction with Aluminum Oxide and Kaolinite." Environ. Sci. Technol., 7, 327-332 (1973b).

Cole, C.V., S.R. Olsen, and C.O. Scott, "The Nature of Phosphate Sorption by Calcium Carbonate." Soil Sci. Soc. Am. Proc., 17, 352-356 (1953).

Coulter Electronics, Inc., "Operator's Reference Manual - Coulter Counter Model ZBI." Hialeah, Florida (1979).

Cowen, W.F., and G.F. Lee, "Phosphorus Availability in Particulate Materials Transported by Urban Runoff." J. Water Pollut. Control Fed., 48, 580-591 (1976a).

Cowen, W.F., and G.F. Lee, "Algal Nutrient Availability and Limitation in Lake Ontario During IFYGL: Part I. Available Phosphorus in Urban Runoff and Lake Ontario Tributary Waters." Ecological Research Series, EPA-600/3-76-094a, 218 pp. (1976b).

DePinto, J.V., J.K. Edzwald, M.S. Switzenbaum, and T.C. Young, "Phosphorus Removal in Lower Great Lakes Municipal Treatment Plants." USEPA Report No. 600/2-80-177, Cincinnati, Ohio (1980).

DePinto, J.V., "An Experimental Apparatus for Evaluating Kinetics of Available Phosphorus Release from Aquatic Particulates." Water Res., 16, 1065-1070 (1982).

DiToro, D.M., "The Effect of Phosphorus Loadings on Dissolved Oxygen in Lake Erie." In: Phosphorus Management Strategies for Lakes, R.C. Loehr, C.S. Martin, and W. Rast (Eds.), Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 191- 205 (1980).

DiToro, D.M., and W.F. Matystik, Jr., "Mathematical Models of Water Quality in Large Lakes, Part 1: Lake Huron and Saginaw Bay." USEPA Report No. 600/3-80-056 (1980).

DiToro, D.M., and J.P. Connolly, "Mathematical Models of Water Quality in Large Lakes, Part 2: Lake Erie." USEPA Report No. 600/3-80-065 (1980).

Dong, A., G.V. Simsiman, and G. Chesters, "Particle-size Distribution and Phosphorus Levels in Soil, Sediment, and Urban Dust and Dirt Samples from the Menomonee River Watershed, Wisconsin, USA." Water Res., 17, 569-577 (1983).

Dorich, R.A., D.W. Nelson, and L.E. Sommers, "Algal Availability of Sediment Phosphorus in Drainage Water of the Black Creek Watershed." J. Environ. Qual., 9, 557-563 (1980).

Edzwald, J.K., D.C. Toensing, and M.C. Leung, "Phosphate Adsorption Reactions with Clay Minerals." *Environ. Sci. Technol.*, *10*, 485-490 (1976).

Fitzgerald, G.P., "Aerobic Lake Muds for the Removal of Phosphorus from Lake Waters." *Limnol. Oceanog.*, *15*, 550-555 (1970).

Frink, C.R., "Chemical and Mineralogical Characteristics of Eutrophic Lake Sediments." *Soil Sci. Soc. Am. Proc.*, *33*, 369-372 (1969).

Golterman, H.L., "Sediments as a Source of Phosphorus for Algae Growth." In: *Interactions Between Sediments and Freshwaters (Proc. SIL-UNESCO Conference)*, H.L. Golterman (Ed.), Junk and Pudoc, The Hague, Netherlands (1976).

Golterman, H.L., C.C. Bakels, and J. Jakolbs-Mogelin, "Availability of Mud Phosphates for the Growth of Algae." *Verh. Int. Ver. Limnol.*, *17*, 467-479 (1969).

Green, D.B., T.J. Logan, and N.E. Smeck, "Phosphate Adsorption-Desorption Characteristics of Suspended Sediments in the Maumee River Basin of Ohio." *J. Environ. Qual.*, *7*, 208-212 (1978).

Griffin, R.A., and J.J. Jurinak, "Kinetics of Phosphate Interaction with Calcite." *Soil Sci. Soc. Am. Proc.*, *38*, 75-79 (1974).

Guillard, R.R.L., and C.J. Lorenzen, "Yellow-Green Algae with Chlorophyllide C." *J. Phycol.*, *8*, 10-14 (1972).

Harms, L.L., J.N. Dornbush, and J.R. Anderson, "Physical and Chemical Quality of Agricultural Land Runoff." *J. Water Pollut. Control Fed.*, *46*, 2460-2470 (1974).

Hegemann, D.A., J.D. Keenan, and A.H. Johnson, "Determination of Particulate-Nutrient Availability." *J. Environ. Eng. Div., Proc. Am. Soc. Civ. Eng.*, *108*, 1312-1325 (1982).

Helyar, K.R., D.N. Munns, and R.G. Burau, "Adsorption of Phosphate by Gibbsite: II. Formation of a Surface Complex Involving Divalent Cations." *J. Soil Sci.*, *27*, 315-323 (1976).

Hieltjes, A.H.M., and L. Lijklema, "Fractionation of Inorganic Phosphates in Calcareous Sediments." *J. Environ. Qual.*, *9*, 405-407 (1980).

Hingston, F.J., R.J. Atkinson, A.M. Posner, and J.P. Quirk, "Specific Adsorption of Anions." *Nature*, *215*, 1459-1461 (1967).

Hingston, F.J., A.M. Posner, and J.P. Quirk, "Anion Adsorption by Goethite and Gibbsite: I. The Role of the Protons in Determining Adsorption Envelopes." *J. Soil Sci.*, *23*, 177-192 (1972).

Hingston, F.J., A.M. Posner, and J.P. Quirk, "Anion Adsorption by Goethite and Gibbsite: II. Desorption of Anions from Hydrous Oxide Surfaces." *J. Soil Sci.*, *25*, 16-26 (1974).

Hsu, P.H., "Adsorption of Phosphate by Aluminum and Iron in Soils." *Soil Sci. Soc. Am. Proc.*, *28*, 474-478 (1964).

Hsu, P.H., "Fixation of Phosphate by Aluminum and Iron in Acidic Soils." *Soil Sci.*, *99*, 398-402 (1965).

Huettl, P.J., R.C. Wendt, and R.B. Corey, "Prediction of Algal-Available Phosphorus in Runoff Suspensions." *J. Environ. Qual.*, *8*, 130-132 (1979).

Kafkafi, U., A.M. Posner, and J.P. Quirk, "Desorption of Phosphate from Kaolinite." *Soil Sci. Soc. Am. Proc.*, *31*, 348-353 (1967).

Keup, L.E., "Phosphorus in Flowing Waters." *Water Res.*, *2*, 373-386 (1968).

Kuo, S., and E.G. Lotse, "Kinetics of Phosphate Adsorption by Calcium Carbonate and Ca-Kaolinite." *Soil Sci. Soc. Am. Proc.*, *36*, 725-729 (1972).

Kuo, S., and E.G. Lotse, "Kinetics of Phosphate Adsorption and Desorption by Lake Sediments." *Soil Sci. Soc. Am. Proc.*, *38*, 50-54 (1974).

Kwolek, J., "Particle Size and Settling Velocity Analysis of Suspended Solids from Four Lake Erie Tributaries." M.S. Thesis, Clarkson College of Technology, Potsdam, NY (1982).

Lam, D.C.L., and J.-M. Jaquet, "Computations of Physical Transport and Regeneraion of Phosphorus in Lake Erie, Fall 1970." *J. Fish. Res. Bd. Can.*, *33*, 550-563 (1976).

Lawler, D.F., "A Particle Approach to the Thickening Process." Ph.D. Dissertation, University of North Carolina, Chapel Hill (1979).

Lerman, A., K.L. Carder, and P.R. Betzer, "Elimination of Fine Suspensions in the Oceanic Water Column." *Earth and Planetary Science Letters*, *37*, 61-70 (1977).

Logan, T.J., "Chemical Extraction as an Index of Bioavailability of Phosphate in Lake Erie Basin Suspended Sediments." LEWMS Report, U.S. Army Corps of Engineers, Buffalo, N.Y., 49 pp. (1978).

Logan, T.J., F.H. Verhoff, and J.V. DePinto, "Biological Availability of Total Phosphorus." LEWMS Report, U.S. Army Corps of Engineers, Buffalo, N.Y., 62 pp. (1979).

Li, W.C., D.E. Armstrong, J.D.H. Williams, R.F. Harris, and J.K. Syers, "Rate and Extent of Inorganic Phosphate Exchange in Lake Sediments." Soil Sci. Soc. Am. Proc., 36, 279-285 (1972).

McCallister, D.L., and T.J. Logan, "Phosphate Adsorption-Desorption Characteristics of Soils and Bottom Sediments in the Maumee River Basin of Ohio." J. Environ. Qual., 7, 87-92 (1978).

Mehta, N.C., J.O. Legg, C.A.I. Goring, and C.A. Black, "Determination of Organic Phosphorus in Soils: I. Extraction Method." Soil Sci. Soc. Am. Proc., 18, 443-449 (1954).

Millard, E.S., C.C. Charlton, and G.A. Burnison, "Availability of Phosphorus in Different Sources Entering the Great Lakes for Algal Growth." Report to Task Group D (Canadian Section), PLUARG, 38 pp. (1979).

Muljadi, D., A.M. Posner, and J.P. Quirk, "The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite and Pseudoboehmite: Part I. The Isotherms and the Effect of pH on Adsorption." J. Soil Sci., 17, 212-229 (1966a).

Muljadi, D., A.M. Posner, and J.P. Quirk, "The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite, and Pseudoboehmite: Part II. The Location of the Adsorption Sites." J. Soil Sci., 17, 230-237 (1966b).

Murphy, J., and J.P. Riley, "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta, 27, 31-36 (1962).

Oloya, T.O., and T.J. Logan, "Phosphate Desorption from Soils and Sediments with Varying Levels of Extractable Phosphate." J. Environ. Qual., 9, 526-531 (1980).

Olsen, S.R., C.V. Cole, F. Watanabe, and L.A. Dean, "Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate." USDA Circular 939 (1954).

Parfitt, R.L., R.J. Atkinson, and R.St.C. Smart, "The Mechanism of Phosphate Fixation by Iron Oxides." Soil Sci. Soc. Am. Proc., 39, 837-841 (1975).

Peters, R.H., "Phosphorus Availability in Lake Memphremagog and its Tributaries." Limnol. Oceanogr., 26, 1150-1161 (1981).

Reddy, M.M., "Sediment Phosphorus Characterization in the Genesee River Watershed, New York." In: Contaminants and Sediments: Volume 2. Analysis, Chemistry, Biology, R.A. Baker (Ed.), Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 119-136 (1980).

Robarge, W.P., and R.B. Corey, "Adsorption of Phosphate by Hydroxy-Aluminum Species on a Cation Exchange Resin." Soil Sci. Soc. Am. J., 43, 481-487 (1979).

Rodel, M.G., D.E. Armstrong, and R.F. Harris, "Sorption and Hydrolysis of Added Organic Phosphorus Compounds in Lake Sediments." Limnol. Oceanogr., 22, 415-422 (1977).

Rodgers, P.W., "Kinetic Studies of Phytoplankton Decomposition." Ph.D. Dissertation, Clarkson College of Technology, Potsdam, NY (1979).

Rodgers, P.W., and D.K. Salisbury, "Modeling Water Quality in Lake Michigan and the Effect of the Anomalous Ice Cover of 1976-1977." A Great Lakes Environmental Planning Study Report, Great Lakes Basin Commission (1981).

Romkens, M.J.M., and D.W. Nelson, "Phosphorus Relationships in Runoff from Fertilized Fields." J. Environ. Qual., 3, 10-14 (1974).

Ross, S.L., "Introduction to Ordinary Differential Equations." Xerox College Publishing, Lexington, Massachusetts (1974).

Ryden, J.C., and J.K. Syers, "Rationalization of Ionic Strength and Cation Effects on Phosphate Sorption by Soils." J. Soil Sci., 26, 395-406 (1975).

Ryden, J.C., J.R. McLaughlin, and J.K. Syers, "Mechanisms of Phosphate Sorption by Soils and Hydrous Ferric Oxide Gel." J. Soil Sci., 28, 72-92 (1977a).

Ryden, J.C., J.K. Syers, and J.R. McLaughlin, "Effects of Ionic Strength on Chemisorption and Potential-Determining Sorption of Phosphate by Soils." J. Soil Sci., 28, 62-71 (1977b).

Sagher, A., "Availability of Soil Runoff Phosphorus to Algae." Ph.D. Dissertation, University of Wisconsin - Madison, 176 pp. (1976).

Salisbury, D.K., J.V. DePinto, and T.C. Young, "Impact of Algal-Available Phosphorus on Lake Erie Water Quality: Mathematical Modeling." USEPA Environmental Research Laboratory - Duluth, Minnesota (1983).

Saunders, W.M.H., "Phosphate Retention by New Zealand Soils and its Relationship to Free Sesquioxides, Organic Matter, and Other Soil Properties." N. Z. J. Agric. Res., 8, 30-57 (1965).

Sharpley, A.N., "The Enrichment of Soil Phosphorus in Runoff Sediments." J. Environ. Qual., 9, 521-526 (1980).

Sharpley, A.N., and J.K. Syers, "Phosphorus Inputs into a Stream Draining an Agricultural Watershed: Amounts and Relative Significance of Runoff Types." Water, Air, Soil Pollut., 9, 417-428 (1979).

Sharpley, A.N., R.G. Menzel, S.J. Smith, E.D. Rhoades, and A.E. Olness, "The Sorption of Soluble Phosphorus by Soil Material During Transport in Runoff from Cropped and Grassed Watersheds." J. Environ. Qual., 10, 211-215 (1981).

Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong, and R.F. Harris, "Sorption of Inorganic Phosphate by Lake Sediments." Soil Sci. Soc. Am. Proc., 35, 244-249 (1971).

Sommers, L.E., R.F. Harris, J.D.H. Williams, D.E. Armstrong, and J.K. Syers, "Fractionation of Organic Phosphorus in Lake Sediments." Soil Sci. Soc. Am. Proc., 36, 51-54 (1972).

Sonzogni, W.C., S.C. Chapra, D.E. Armstrong, and T.J. Logan, "Bioavailability of Phosphorus Inputs to Lakes." J. Environ. Qual., 11, 555-563 (1982).

Sugarman, R.J., "Conference Objectives." In: Phosphorus Management Strategies for Lakes, R.C. Loehr, C.S. Martin, and W. Rast (Eds.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 7-10 (1980).

Syers, J.K., and T.W. Walker, "Phosphorus Transformations in a Chronosequence of Soils Developed on Wind-Blown Sand in New Zealand: I. Total and Organic Phosphorus." J. Soil Sci., 20, 57-64 (1969).

Syers, J.K., M.G. Browman, G.W. Smillie, and R.B. Corey, "Phosphate Sorption by Soils Evaluated by the Langmuir Adsorption Equation." Soil Sci. Soc. Am. Proc., 37, 358-363 (1973).

Task Group III, "Fifth Year Review of Canada-United States Water Quality Agreement." Report of Task Group III, A Technical Group to Review Phosphorus Loadings, U.S. Department of State, Washington, D.C. (1978).

Thomann, R.V., D.M. DiToro, R.P. Winfield, and D.J. O'Connor, "Mathematical Modeling of Phytoplankton in Lake Ontario: I. Model Development and Verification." USEPA Report No. 600/3-75-005, Ecological Research Series, Large Lakes Research Lab, Grosse Ile, Michigan (1975).

Thomas, H.A., Jr., "Graphical Determination of BOD Curve Constants." Water and Sewage Works, 97, 123 (1950).

U.S. Army Corps of Engineers, "Lake Erie Wastewater Management Study - Final Report." Buffalo, N.Y. (1982).

Verhoff, F.H., and D.A. Melfi, "Total Phosphorus Transport During Storm Events." J. Environ. Eng. Div., Proc. Am. Soc. Civ. Eng., 104, 1021-1026 (1978).

Verhoff, F.H., D.A. Melfi, and S.M. Yaksich, "Storm Travel Distance Calculations for Total Phosphorus and Suspended Materials in Rivers." Water Resour. Res., 15, 1354-1360 (1979).

Verhoff, F.H., M. Heffner, and W.A. Sack, "Measurement of Availability Rates for Total Phosphorus from River Waters." LEWMS Technical Report, U.S. Army Corps of Engineers, Buffalo, N.Y. (1978).

Weaver, R.M., "A Simplified Determination of Reductant-Soluble Phosphate in Soil Phosphate Fractionation Schemes." Soil Sci. Soc. Am. Proc., 38, 153-154 (1974).

Wentz, D.A., and G.F. Lee, "Sedimentary Phosphorus in Lake Cores - Observations on Depositional Pattern in Lake Mendota." Environ. Sci. Technol., 3, 754-759 (1969).

Wildung, R.E., and R.L. Schmidt, "Phosphorus Release from Lake Sediments." USEPA Report No. EPA-R3-73-024, 185 pp. (1973).

Williams, J.D.H., and T.W. Walker, "Fractionation of Phosphate in a Maturity Sequence of New Zealand Basaltic Soil Profiles: I." Soil Sci., 107, 22-30 (1969).

Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris, and D.E. Armstrong, "Levels of Inorganic and Total Phosphorus in Lake Sediments as Related to Other Sediment Parameters." Environ. Sci. Technol., 5, 1113-1120 (1971a).

Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong, "Fractionation of Inorganic Phosphate in Calcareous Lake Sediments." Soil Sci. Soc. Am. Proc., 35, 250-255 (1971b).

Williams, J.D.H., J.K. Syers, D.E. Armstrong, and R.F. Harris, "Characterization of Inorganic Phosphate in Noncalcareous Lake Sediments." Soil Sci. Soc. Am. Proc., 35, 556-561 (1971c).

Williams, J.D.H., J.M. Jaquet, and R.L. Thomas, "Forms of Phosphorus in the Surficial Sediments of Lake Erie." J. Fish. Res. Bd. Can., 33, 413-429 (1976a).

Williams, J.D.H., T.P. Murphy, and T. Mayer, "Rates of Accumulation of Phosphorus Forms in Lake Erie Sediments." J. Fish. Res. Bd. Can., 33, 430-439 (1976b).

Williams, J.D.H., H. Shear, and R.L. Thomas, "Availability to *Scenedesmus quadricauda* of Different Forms of Phosphorus in Sedimentary Materials from the Great Lakes." Limnol. Oceanogr., 25, 1-11 (1980a).

Williams, J.D.H., T. Mayer, and J.O. Nriagu, "Extractability of Phosphorus from Phosphate Minerals Common in Soils and Sediments." Soil Sci. Soc. Am. J., 44, 462-465 (1980b).

Young, T.C., J.V. DePinto, S.E. Flint, M.S. Switzenbaum, and J.K. Edzwald, "Algal Availability of Phosphorus in Municipal Wastewater." J. Water Pollut. Control Fed., 54, 1505-1516 (1982).

BIBLIOGRAPHY OF RELATED PUBLICATIONS

Bollenbacher, M., "Ion Exchange Resins as Estimators of Algal-Available Sediment Phosphorus from Five Lower Great Lakes Tributaries." M.S. Thesis, Clarkson College of Technology, Potsdam, NY (1981).

DePinto, J.V., T.C. Young, and S.C. Martin, "Algal-Available Phosphorus in Suspended Sediments from Lower Great Lakes Tributaries." *J. Great Lakes Res.*, *7*, 311-325 (1981)

DePinto, J.V., T.C. Young, S.C. Martin, and J.S. Bonner, "Release of Available Phosphorus from Particulate Matter in the Great Lakes." Submitted to *J. Great Lakes Res.* (1983).

Victore, A.M., "Physical and Chemical Characterization of Algal-Available Phosphorus in Suspended Sediments from Lower Great Lakes Tributaries." M.S. Thesis, Clarkson College of Technology, Potsdam, NY (1981).

Young, T.C., and J.V. DePinto, "Algal-Availability of Particulate Phosphorus from Diffuse and Point Sources in the Lower Great Lakes Basin." in *Sediment/Freshwater Interaction*, P.G. Sly (ed.), Dr W. Junk Publishers, 111-119 (1982).

APPENDIX A

THE POWER LAW FUNCTION AND RELATED EQUATIONS

In analyzing polydisperse suspensions, a mathematical description of the distribution of particle sizes is often useful. The three most common measures of particle size are particle diameter (d_p), surface area (S), and volume (V). An example of a particle size distribution based on particle volume is shown in Figure A-1. In this plot, the cumulative number concentration (N), in units of number/cm^3 , is equal to the total concentration of particles with a volume equal to or less than V (μm^3). Alternatively, the distribution of particle sizes could be represented by a plot of N versus d_p or S. The slopes of these curves can be described by mathematical expressions known as particle size distribution functions (Lawler, 1979). These functions may be defined as follows:

$$\Delta N/ \Delta V = dN/dV = n(V) \qquad (\text{number}/cm^3\text{,}\mu m^3) \qquad (A.1)$$

$$\Delta N/ \Delta S = dN/dS = n(S) \qquad (\text{number}/cm^3\text{,}\mu m^2) \qquad (A.2)$$

$$\Delta N/\Delta d_p = dN/d(d_p) = n(d_p) \qquad (\text{number}/cm^3\text{,}\mu m) \qquad (A.3)$$

where n(V), n(S), and n(d_p) represent the particle size distribution functions.

As was mentioned in the text of Chapter 3, for aquatic suspensions, the particle size distribution function often takes the form:

$$n(d_p) = A\, d_p^{-\beta} \qquad (A.4)$$

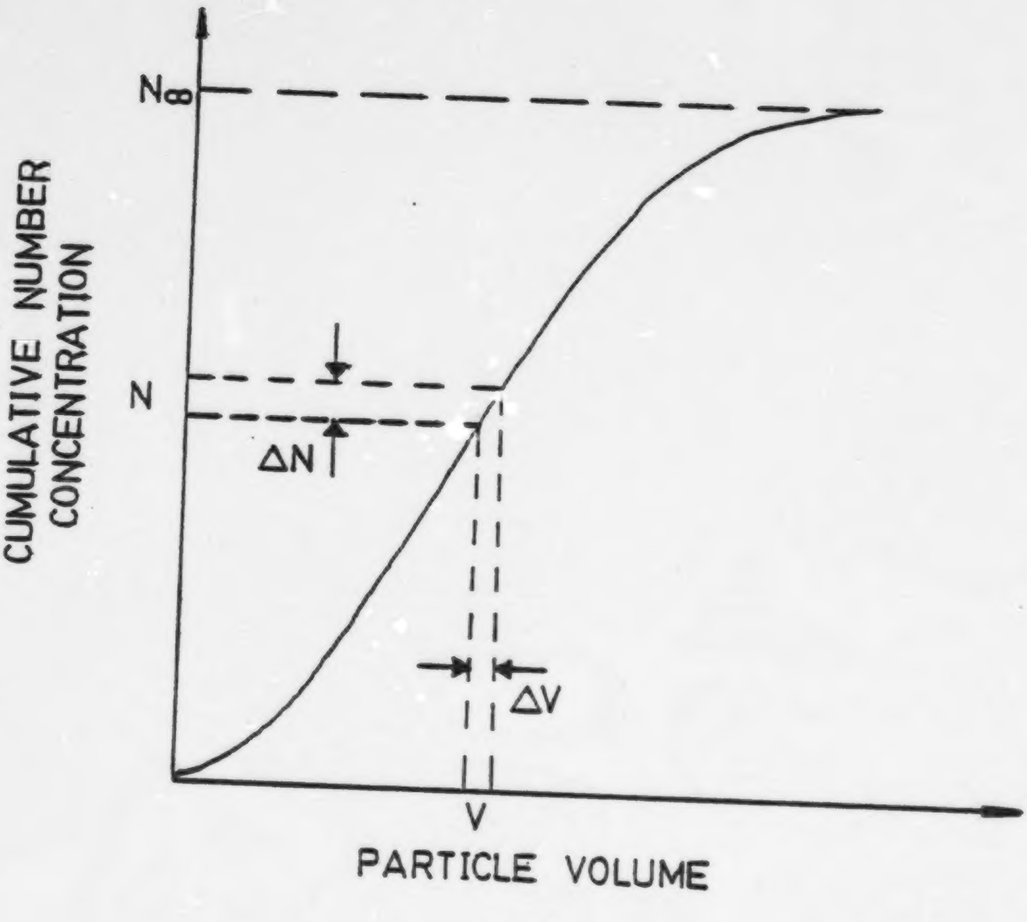


Figure A-1. Hypothetical particle size distribution (from Lawler, 1979).

where A = a coefficient related to the total particle concentration;

and β = the power law exponent.

The value of β for a particular sample may be determined experimentally from the slope of a log-log plot of $n(d_p)$ versus d_p. For naturally occurring particles, values of β typically range from 2 to 5 (Lawler, 1979). Smaller values of β are characteristic of samples that contain a relatively large proportion of coarse-grained particles. Samples containing higher concentrations of fine-grained particles exhibit steeper slopes for log-log plots of $dN/d(d_p)$ vs. d_p, and thus, higher values of β.

Lawler (1979) used Equation A.4, known as the power law function, and the assumption that particles were spherical in shape to derive the following relationships:

$$\frac{dV}{d(\log d_p)} = \frac{2.3\pi}{6} A \cdot d_p^{(4-\beta)} \qquad (A.5)$$

$$\frac{dS}{d(\log d_p)} = 2.3\pi A \cdot d_p^{(3-\beta)} \qquad (A.6)$$

$$\frac{dN}{d(\log d_p)} = 2.3 A \cdot d_p^{(1-\beta)} \qquad (A.7)$$

These equations can provide insights into the significance of β values in terms of the distribution of particle volume, surface area, and number among the range of particle diameters investigated. The results are particularly interesting when the exponent of d_p in one of these equations is equal to zero (i.e. when β = 1, 3, or 4). Plots of the left-hand sides of Equations A.5-A.7 versus log d_p for β values of 1, 3, and 4 are shown in Figure A-2.

A suspension that can be descibed by the power law function with an exponent, β, of 1.0 would have an equal number of particles in each logarithmic size interval. This is demonstrated by the horizontal line for particle number

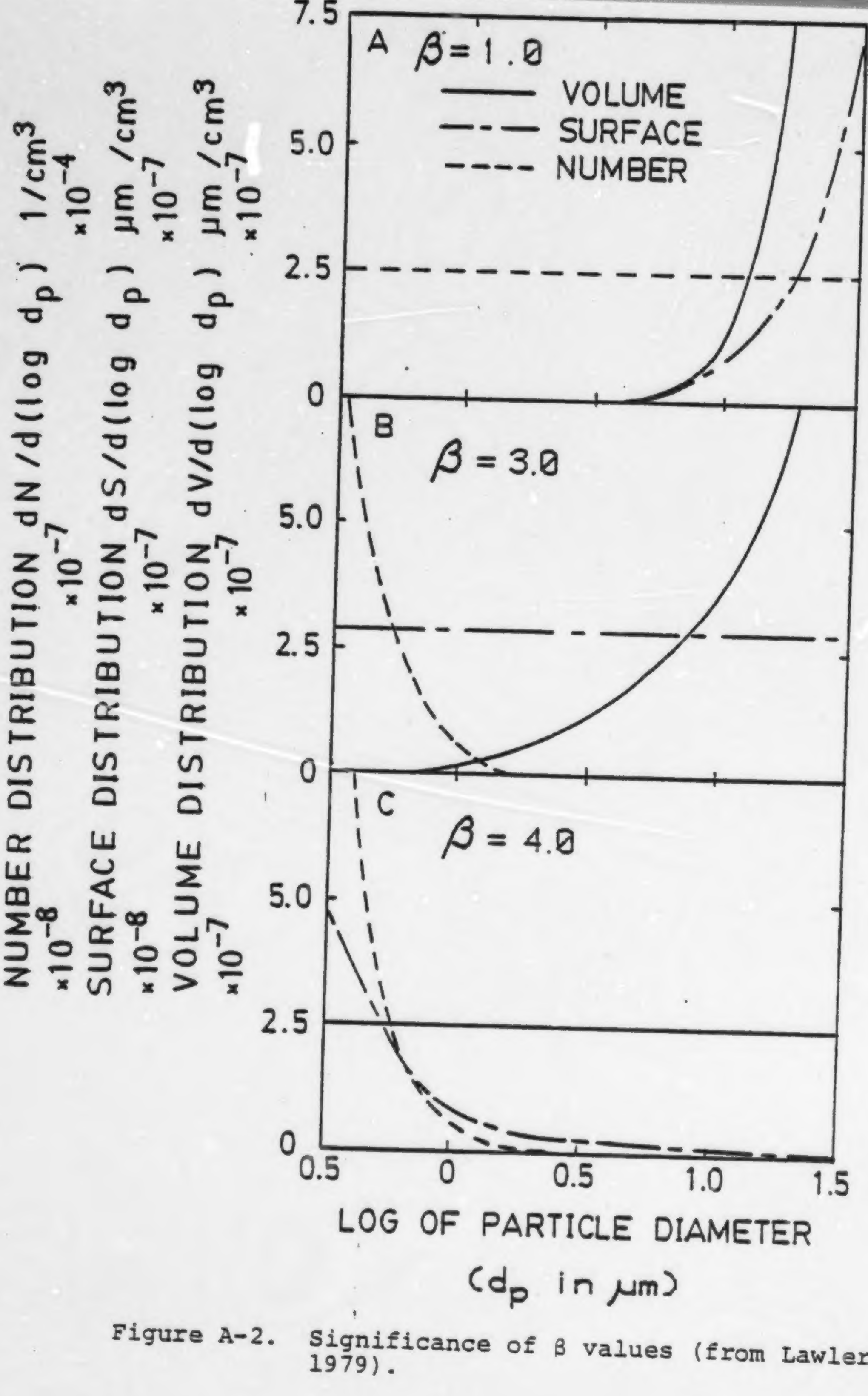


Figure A-2. Significance of β values (from Lawler, 1979).

distribution in Figure A-2a. In such a suspension, the coarser sized particles would make a greater contribution to the total particle volume and surface area than the smaller diameter particles.

From Figure A-2b, it can be seen that, for a sample with a particle size distribution characterized by a β value of 3.0, the total particle surface area is uniformly distributed among the various size intervals. In this case, the total number of particles in the suspension is concentrated in the fine-grained region of the particle size distribution, while the coarse-sized fractions account for the majority of the total particle volume.

Finally, as shown in Figure A-2c, a particle suspension exhibiting a β value of 4.0 would have the total particle volume equally distributed throughout all of the logarithmic size intervals. Also, both the total particle number and surface area would be predominately associated with the finer-sized fractions of the size distribution. Thus, experimental evaluation of the power law exponent, β, for a sample can provide useful information on the contribution of various particle size (diameter) fractions to the total volume, surface area, or number of particles in the suspension.

APPENDIX B

DETERMINATION OF DIFFUSION COEFFICIENT FOR THE DCDA

Two experiments were conducted to provide data for the calculation of a diffusion coefficient for the DCDA reactors used for bioassays in this study. In both cases, a series of DCDAs was assembled and the dark side of each was filled with deionized water and spiked with a known concentration of soluble orthophosphate. For the first experiment, the opposite side of each reactor was filled with deionized water containing no soluble phosphate. In the second experiment, 400 ml of a one week old P-starved (25 µgP/l) culture of *Selenastrum capricornutum* was added to the light side. The DCDAs were stirred continuously on a magnetic stir table for various lengths of time. The reactors were then sampled and the soluble P levels in both vessels were determined. Diffusion rates were calculated according to the mathematical analyses presented below.

FIRST EXPERIMENT

Theory

A mass balance on P in the spiked vessel yields:

$$dP_s/dt = -\alpha (P_s - P_u) \qquad (B.1)$$

where P_s = soluble phosphorus concentration on the spiked side (µg/l);

P_u = soluble phosphorus concentration on the unspiked side (µg/l);

and α = the bulk diffusion coefficient (day^{-1}).

Since no soluble P sink was present in the first diffusion experiment, the total mass of soluble P must be conserved. So,

$$V_s P_s + V_u P_u = V_s P_o \qquad (B.2)$$

where V_s, V_u = volumes of spiked and unspiked vessels, respectively;

and P_o = initial soluble P concentration in spiked side (μg/l).

Since $V_s = V_u = 400$ ml, $P_s + P_u = P_o$, or

$$P_u = P_o - P_s \tag{B.3}$$

Thus, Equation B.1 can be rewritten as

$$dP_s/dt = -\alpha\,(2P_s - P_o) \tag{B.4}$$

or,

$$dP_s/dt + 2\,\alpha\,P_s = \alpha\,P_o \tag{B.5}$$

Using the initial condition that $P_s = P_o$ at $t = 0$ to evaluate the constant of integration, this linear first-order differential equation is found to have the solution:

$$P_s = P_o/2\ (1 + e^{-2\alpha t}) \tag{B.6}$$

Based on Equation B.6, a plot of $\ln\,(2P_s/P_o - 1)$ versus t should have a slope of $-2\,\alpha$.

Results and Calculations

The results of the first diffusion experiment are presented in Table B-1 and are also shown graphically in Figure B-1. These data indicate that diffusion is consistent from one DCDA to the next and that the vessels are approaching an equilibrium level of 125 μgP/l at a rapid rate. Regression analysis of $\ln\,(2P_s/P_o - 1)$ vs. t yields a straight line with a slope $= -4.131$ day^{-1} and a correlation coefficient, $r = -0.971$. Therefore, the bulk diffusion coefficient, α, for these DCDA systems was 2.065 day^{-1}. Predicted values of P_s based on equation B.6 with $\alpha = 2.065$ day^{-1} and $P_o = 250$ μg/l are plotted along with the observed data in Figure B.1.

TABLE B-1. RESULTS OF FIRST DCDA DIFFUSION EXPERIMENT

	Time of sampling		Measured SRP conc. at sampling		
DCDA #	hours	days	Spiked side (P_s)	Unspiked side (P_u)	$\ln((2P_s/P_o)-1)$
-	0	0	250 μg/l	0 μg/l	0
1	4.75	0.198	175.6	76.7	-0.904
2	4.75	0.198	170.5	74.4	-1.011
3	7.0	0.292	159.9	88.2	-1.276
4	10.0	0.417	152.1	98.6	-1.529
5	10.0	0.417	142.0	105.6	-1.995

- Initial SRP concentration on spiked side, P_o = 250 μg/l.

- Contents of unspiked side - Deionized water.

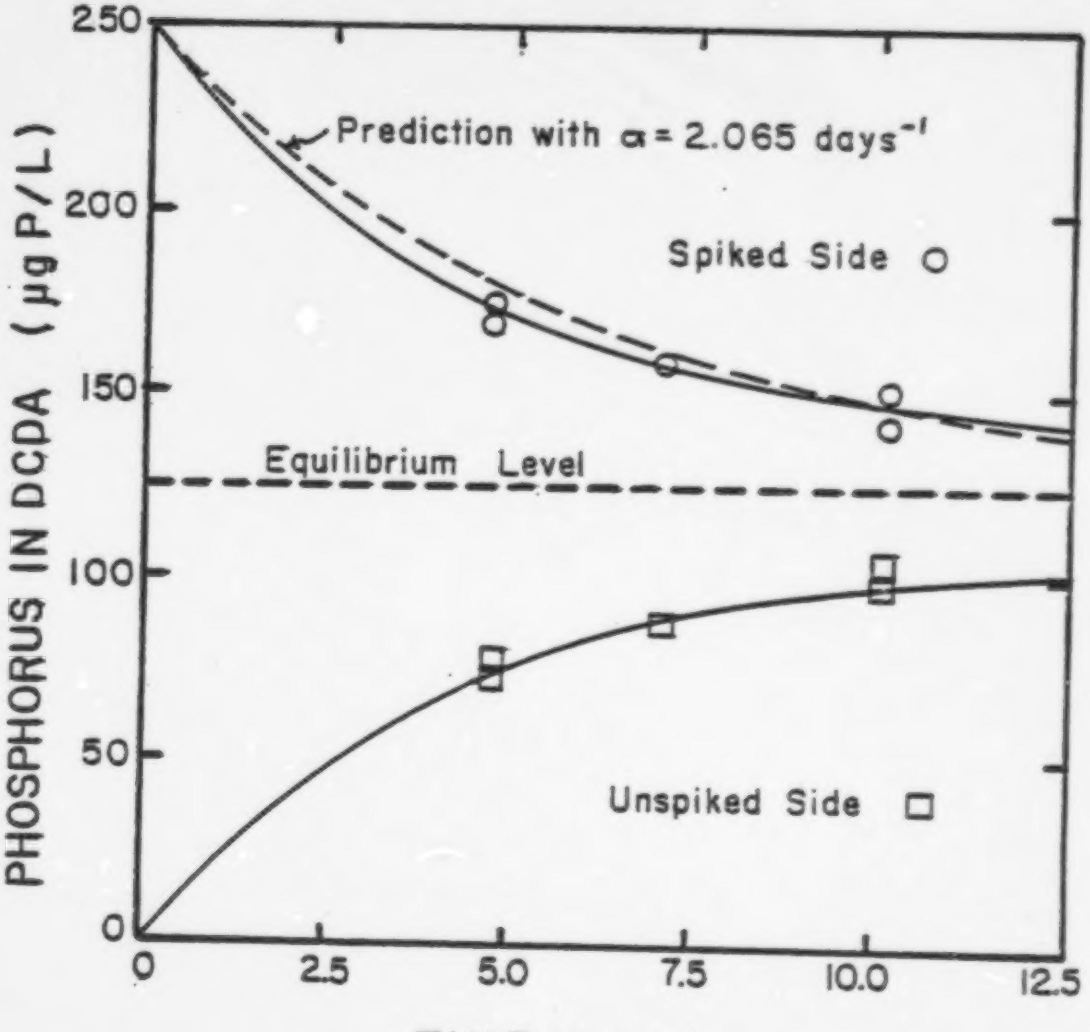


Figure B-1. Results of first DCDA diffusion experiment.

SECOND EXPERIMENT

Theory

For the second experiment, in which the unspiked sides of the DCDAs contained P-starved *Selenastrum*, Equation B.1 again results from a mass balance on soluble P in the spiked vessel. That is,

$$dP_s/dt = - \alpha (P_s - P_u) \tag{B.1}$$

However, since the algae represent a sink of soluble P, it is not possible to simplify this using the conservation of mass equation as in the first experiment. Equation B.1 can be rearranged to the form:

$$dP_s/dt + \alpha P_s = \alpha P_u \tag{B.7}$$

Assuming that the algal culture maintains P_u at a relatively low and constant level, this may be solved as a linear, first-order differential equation. Again using the condition that $P_s = P_o$ at $t = 0$, the solution to this equation is found to be:

$$(P_s - P_u) = (P_o - P_u)\, e^{-\alpha t} \tag{B.8}$$

The bulk diffusion coefficient, α, may be determined from a plot of $\ln [(P_s - P_u)/(P_o - P_u)]$ versus t. This plot should yield a straight line with a slope of $-\alpha$.

Results and Calculations

The results of the second diffusion experiment are presented in Table B-2. The difference between the initial spike of 125 µgP/l and the sum of the last two columns in Table B-2 represents the amount of phosphorus taken up by the algae on the unspiked side of the DCDAs. Based on the nonzero SRP concentrations observed in the unspiked vessels, it appears that as a result of the large P spike and high diffusion rate, P was supplied to the algae faster than it could be taken up. The value of P_u does decrease steadily with time, however, indicating that this condition is a transient one.

From the data in the last column of Table B-2, the assumption that P_u = constant = 10 µg/l appears to be reasonable

TABLE B-2. RESULTS OF SECOND DCDA DIFFUSION EXPERIMENT

DCDA #	Incubation time (hours)	SRP on spiked side after incubation, P_s (µg P/l)	SRP on unspiked side after incubation, P_u (µg P/l)
1	4.42	77.5	13.5
2	4.42	78.5	22.4
3	8.26	62.3	11.8
4	8.26	66.2	14.6
5	12.0	47.5	13.6
6	12.0	50.4	13.6
7	20.0	29.1	10.1
8	20.0	26.6	10.1

- Initial SRP concentration on spiked side, P_s = 125 µg/l.

Note: Initial SRP concentration on unspiked side was 0.3 µg/l.

for this experiment. Thus, a plot of ln $[(P_s - 10)/(P_o - 10)]$ versus t should give a straight line with a slope of $-\alpha$. Plotting the data in Table B.2 in this manner results in a bulk diffusion coefficient, $\alpha = 2.105\ \text{day}^{-1}$ and a linear correlation coefficient, $r = -0.9917$. This value is very close to that obtained in the first diffusion experiment.

MOLECULAR DIFFUSION COEFFICIENT

The bulk diffusion coefficient, α, for the DCDAs may be related to the molecular diffusion coefficient, D_m, by the expression:

$$\alpha = D_m A / \sigma V \qquad \text{(B.9)}$$

where D_m = molecular diffusion coefficient (cm^2/day)

A = open pore area in the membrane (cm^2)
σ = thickness of the membrane (cm)

and V = volume of liquid in the spiked vessel (cm^3).

By rearranging this to the form of Equation B.10, D_m may be calculated from the value of α obtained in the diffusion studies.

$$D_m = \sigma \alpha V/A \qquad \text{(B.10)}$$

For the DCDA reactors used in this study, $V = 400\ \text{cm}^3$. The Nuclepore polycarbonate membranes used to separate the two vessels of the DCDAs have a thickness, $\sigma = 10^{-3}$ cm and a pore density of 10^8 pores/cm^2. The value of D_m calculated using this information and $\alpha = 2.065\ \text{day}^{-1}$ is $0.218\ \text{cm}^2/\text{day}$, or $2.52 \times 10^{-6}\ \text{cm}^2/\text{sec}$, which is definitely within the typical range for molecular diffusion of salts in water (DePinto, 1982).

APPENDIX C

DERIVATION OF AN EQUATION FOR PHOSPHORUS UPTAKE BY ALGAE ON THE ASSAY SIDE OF DCDA REACTORS (BASED ON DEPINTO, 1982)

A mass balance for soluble phosphorus on the sediment vessel of the DCDA results in the following equation:

$$\begin{pmatrix}\text{Accumulation rate}\\ \text{of soluble P}\end{pmatrix} = \begin{pmatrix}\text{Rate of release}\\ \text{from sediments}\end{pmatrix} - \begin{pmatrix}\text{Rate of diffusion}\\ \text{across membrane}\end{pmatrix}$$

or

$$V \frac{dC_1}{dt} = W(t) - V\alpha C_1 \qquad (C.1)$$

where C_1 = Soluble P concentration in sediment vessel ($\mu g/\ell$).

$W(t)$ = Rate of P release from sediments (μg/day).

V = Sediment vessel volume (ℓ).

α = Bulk diffusion coefficient for soluble P across the DCDA membrane (days^{-1}).

If the bioavailable sediment P is released at a first-order rate in the sediment vessel, then

$$P_{rel}(t) = P_{ult}(1-e^{-k_r t}) \qquad (C.2)$$

where $P_{rel}(t)$ = the quantity of P released form the sediments at time t (μgP/g sediment)

P_{ult} = the total amount of P released from the sediments at $t=\infty$ (μgP/g sediment)

and k_r = the first-order sediment P release rate (days^{-1}).

The rate of release is given by:

$$W(t) = m \frac{dP_{rel}(t)}{dt} = m\, k_r\, P_{ult}\, e^{-k_r t} \qquad (C.3)$$

where m = total mass of sediments in the sediment vessel (g).

Substituting Equation C.3 into C.1 and rearranging terms:

$$V \frac{dC_1}{dt} + V\alpha C_1 = m\ k_r\ P_{ult}\ e^{-k_r t} \tag{C.4}$$

Since $Q_1 = \frac{C_1 V}{m}$ = the quantity of P that has been released from the sediments, but remians in the sediment vessel (μgP/g sediment)

if all terms in Equaiton C.4 are divided by m, the result is

$$\frac{dQ_1}{dt} + \alpha Q_1 = k_r\ P_{ult}\ e^{-k_r t} \tag{C.5}$$

Applying an integrating factor of $e^{\alpha t}$ gives the solution:

$$Q_1 = \frac{k_r\ P_{ult}}{(\alpha - k_r)}\ e^{-k_r t} + C\ e^{-\alpha t} \tag{C.6}$$

Using the initial condition that $Q_1=0$ at $t=0$ to solve for C, this becomes

$$Q_1(t) = \frac{k_r\ P_{ult}}{(\alpha - k_r)}\ (e^{-k_r t} - e^{-\alpha t}) \tag{C.7}$$

Performing a mass balance for particulate (algal) P on the assay side of the DCDA yields:

(Rate of accumulation of algal P) = (Rate of diffusion across membrane)

or

$$V \frac{dC_2}{dt} = V\alpha C_1 \tag{C.8}$$

where C_2 = the concentration of algal particulate P in the assay vessel that originated as sediment P in the sediment vessel (μg/ℓ).

Using the relationships:

$\frac{C_2 V}{m} = Q_2$ = the quantity of P released from the sediments and taken up by the algae on the assay side (μgP/g sediment)

and $Q_1 = \frac{C_1 V}{m}$,

if both sides of Equation C.8 are divided by m, then

$$\frac{dQ_2}{dt} = \alpha Q_1 \qquad (C.9)$$

Substituting Equation C.7 into C.9 gives:

$$\frac{dQ_2}{dt} = \frac{\alpha k_r \, P_{ult}}{(\alpha - k_r)} e^{-k_r t} - \frac{\alpha k_r \, P_{ult}}{(\alpha - k_r)} e^{-\alpha t} \qquad (C.10)$$

Integration and application of the initial condition $Q_2=0$ at $t=0$ yields the solution:

$$Q_2(t) = \frac{\alpha \, P_{ult}}{(\alpha - k_r)} (1-e^{-k_r t}) - \frac{k_r \, P_{ult}}{(\alpha - k_r)} (1-e^{-\alpha t}) \qquad (C.11)$$

For cases where $\alpha \gg k_r$,

$$\frac{\alpha}{(\alpha - k_r)} \equiv 1 \text{ and } \frac{k_r}{(\alpha - k_r)} \approx 0$$

and Equation C.11 may be simplified to

$$Q_2(t) = P_{ult}(1-e^{-k_r t}) \qquad (C.12)$$

The right-hand side of this equation is identical to Equation C.2. This indicates that, provided the diffusion rate is much greater than the sediment P release rate, algal uptake of P on the assay side can be used directly as a measurement of sediment P release in the regeneration vessel.

TABLE D-1. RESULTS OF PHYSICAL AND CHEMICAL MEASUREMENTS ON UNFILTERED TRIBUTARY SAMPLES AND FILTRATES

Tributary and sample no.	Flow* (m^3/s)	pH	Filtrate alkalinity (mg/ℓ as CaCO$_3$)	Suspended solids (mg/ℓ)		Phosphorus concs. (µg/ℓ)		
				Total†	%<20µm	TP	TSP	SRP
Maumee River:								
5	803.	7.35	105.9	390.	97.8	841.	133.3	109.4
8	872.	7.80	91.1	421.	96.6	602.	97.5	88.2
13	691.	8.13	137.6	278.	93.9	437.	102.5	93.1
15	118.	8.13		55.5		188.	103.	95.7
17	348.	7.84		111.		266.	99.9	107.8
19	898.	7.82	166.3	453.	83.7	668.	145.3	120.5
21	339.	8.11	96.5	348.	98.6	496.	124.4	99.5
27	578.2			146.	45.9	312.5	114.4	88.1
41	246.7			146.2		279.0	100.9	91.1
42	345.2			149.0		272.0	120.0	111.2
50	1878.0			918.		1152.0	88.4	66.5
Sandusky River:								
2	566.	7.60	48.5	1028.	96.1	1350.	129.0	99.9
7	362.	7.69	69.3	690.	96.1	875.	91.5	83.3
11	245.	7.60	94.0	557.	96.2	624.	77.4	59.2
16	59.1	7.83	103.9	535.	94.8	686.	97.3	83.9
18	73.5			72.		165.	60.8	57.7
20	257.	7.62	30.2	1020.	95.0	1030.	74.8	56.8
24	22.5	8.22	153.4	183.		302.	107.8	95.6
25	60.1	8.30	130.7	432.		530.	86.1	77.1
26	240.2			520.	77.8	749.	125.6	96.9
28	161.8			247.	83.0	440.5	120.6	104.8
30	43.3			105.	74.3	196.5	56.1	40.7
31	85.1			131.	61.8	291.5	91.0	77.5
34	101.4			220.	83.2	365.5	90.4	71.0
35	102.0			232.	77.2	398.5	82.6	69.5
36	50.8			205.		362.5	86.2	77.3

(continued)

TABLE D-1 (continued)

Tributary and sample no.	Flow* (m^3/s)	pH	Filtrate alkalinity (mg/ℓ as CaCO$_3$)	Suspended solids (mg/ℓ) Total†	Suspended solids (mg/ℓ) %<20μm	Phosphorus concs. (μg/ℓ) TP	Phosphorus concs. (μg/ℓ) TSP	Phosphorus concs. (μg/ℓ) SRP
Sandusky River:								
37	31.0			123.		248.5	56.6	45.8
38A	85.5			129.		204.5	73.3	62.6
38	122.2			212.5		359.0	83.9	63.0
39	136.0			268.7		425.0	80.8	66.5
40	189.4			223.7		366.0	86.7	83.4
44**	419.9			3753.		3890.0	59.4	47.5
45	383.1			1432.		1581.0	72.9	61.5
46**	282.2			1095.		1271.0	83.1	62.5
47	206.3			574.		831.0	81.2	68.4
49	630.3			3120.		3222.0	50.4	41.7
51	576.2			1002.		1205.0	36.2	22.7
52	521.9			838.		1023.0	46.4	30.4
Cuyahoga River:								
1	142.	7.55	66.3	590.	70.8	716.	39.5	32.1
4	133.	7.37	67.3	278.	66.9	446.	51.4	30.7
12	130.	7.60	62.4	195.	58.5	303.	75.3	47.8
14	10.8	7.71		12.0		275.	160.	157.7
29	127.0			206.	52.9	321.0	63.4	48.1
Cattaraugus (S. Br.):								
6	64.3	7.63	47.5	4325.	48.2	2825.	11.4	11.4
9	32.6	7.38	43.6	647.	64.8	346.	14.6	4.2
10	8.10	8.05	65.3	150.	75.3	101.	10.8	3.9
22	12.4	8.26	100.0				16.6	5.0
23	30.0	7.70	82.7				16.1	6.9

(continued)

TABLE D-1 (continued)

Tributary and sample no.	Flow* (m^3/s)	pH	Filtrate alkalinity (mg/ℓ as $CaCO_3$)	Suspended solids (mg/ℓ)		Phosphorus concs. (μg/ℓ)		
				Total†	%<20μm	TP	TSP	SRP
Genesee River:								
3		7.35	80.2	156.	88.5	192.	37.0	18.3
Honey Creek:								
32	25.8			404.	89.1	679.0	165.2	145.0
33	14.6			220.	94.5	398.5	98.6	79.2
43	53.7			815.		1115.0	75.4	56.4
48	112.0			2130.		2094.0	46.1	38.8

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* Values given are instantaneous flows at time of sample collection, except those for the Cuyahoga River, which are average daily flows.

† Amount retained on a membrane filter with a pore size of 0.45 μm.

** Due to leaks in the cubitainers in which samples #44 and 46 were shipped, the total suspended solids and TP concentrations listed are probably somewhat high.

TABLE D-2. RESULTS OF P FRACTIONATION STUDIES ON TRIBUTARY SUSPENDED SEDIMENTS

Sample no.	T-Sed-P	(TP-TSP) SS	Concentrations in µgP/g sediment T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
Maumee River								
5	1,181	1,815	289	203	86	292	107	121
8	1,362	1,198	412	284	128	244	73	155
13	1,118	1,203	363	225	138	218	126	69
19	1,286	1,154	304	227	77	250	125	131
21	1,088	1,068	278	223	56	171	75	134
27	1,682	1,357	710	376	334	301	141	162
41	1,205	1,218	438	315	123	211	123	278
42	1,258	1,020	428	312	116	205	195	275
50	1,149	1,159	406	289	117	252	87	240
Mean (1980)	1,207		329	232	97	235	101	122
Mean (1981)	1,323		495	323	172	242	136	239
Mean (All)	1,259	1,244	403	273	131	238	117	174
Mean (% of T-Sed-P)			32.0	21.7	10.4	18.9	9.3	13.8
Sandusky River								
2	1,253	1,188	451	259	192	-	75	165
7	1,319	1,136	422	287	135	215	55	143
11	1,071	981	367	249	118	217	58	123
16	1,209	1,100	395	249	146	272	53	30
20	940	936	318	227	91	143	43	102
25	1,057	1,028	232	155	77	337	56	89
26	1,299	1,199	479	379	100	262	138	297
28	1,366	1,295	517	389	128	270	118	312
30	1,405	1,251	578	369	209	245	105	125
31	1,373	1,531	637	355	282	335	105	146
34	1,232	1,250	563	359	204	238	82	129
35	1,260	1,362	525	290	235	249	87	124
36	1,276	1,348	406	265	141	298	75	147
37	1,309	1,560	509	319	190	251	80	143
38A	1,316	1,017	498	332	166	238	101	300

(continued)

TABLE D-2 (continued)

Sample no.	T-Sed-P	(TP-TSP) / SS	Concentrations in µgP/g sediment					
			T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
Sandusky River (cont'd.)								
38	1,214	1,295	508	373	135	211	113	291
39	1,241	1,281	516	357	159	212	118	299
40	1,239	1,249	542	369	173	217	100	287
44	936	1,021	336	208	128	120	58	285
45	1,018	1,053	393	277	116	180	57	295
46	1,055	1,085	406	284	122	225	55	268
47	1,172	1,306	465	330	135	278	71	185
49	974	1,017	350	229	121	217	44	196
51	1,078	1,166	407	278	129	232	48	194
52	1,100	1,165	394	256	138	235	46	202
Mean (1980)	1,141		364	238	126	237	57	109
Mean (1981)	1,203		475	317	158	238	83	221
Mean (All)	1,188	1,193	449	298	151	237	77	194
Mean (% of T-Sed-P)			37.7	25.1	12.7	20.0	6.5	16.3
Cuyahoga River								
1	1,294	1,147	518	339	178	-	196	108
4	1,310	1,419	513	420	92	322	176	77
12	1,229	1,168	593	442	152	287	200	6
29	1,426	1,250	677	568	109	230	180	102
Mean (1980)	1,278		541	400	141	304	191	64
Mean (All)	1,315	1,246	575	441	133	280	188	73
Mean (% of T-Sed-P)			43.8	33.6	10.1	21.3	14.3	5.6
Genesee River								
3	957	994	240	170	69	187	273	77
% of T-Sed-P			25.1	17.8	7.2	19.5	28.5	8.0

(continued)

TABLE D-2 (continued)

Sample no.	T-Sed-P	(TP-TSP) SS	T-NaOH-P	R-NaOH-P	NR-NaOH-P	CDB-P	HCl-P	Residual P
			Concentrations in μgP/g sediment					
Cattaraugus Creek								
6	604	651	111	59	52	57	242	49
9	673	512	79	51	28	88	308	55
10	733	601	76	51	25	70	348	46
22	624		40	26	14	105	303	44
23	549		73	43	30	88	323	47
Mean (All)	637	588	76	46	30	82	305	48
Mean (% of T-Sed-P)			11.9	7.2	4.7	12.9	47.9	7.5
Honey Creek								
32	1,346	1,272	588	426	162	201	76	307
33	1,367	1,363	585	423	162	262	85	305
43	1,054	1,276	449	322	127	152	37	263
48	988	961	398	254	144	198	27	184
Mean (All)	1,189	1,218	505	356	149	203	56	265
Mean (% of T-Sed-P)			42.5	30.0	12.5	17.1	4.7	22.3
Detroit River								
*	1,424		596	305	291	177	323	170
% of T-Sed-P			41.9	21.4	20.4	12.4	22.7	11.9

* Sediments were composited from 4 sampling locations.

APPENDIX E

EQUATIONS AND COMPUTER ALGORITHM USED IN CALCULATING TWO-COMPONENT SEDIMENT P RELEASE COEFFICIENTS

In this study, two-component release of sediment P was first assumed to follow the equation:

$$P_{rel}(t) = P_r(1-e^{-k_{rr}t}) + P_s(1-e^{-k_{sr}t}) \tag{11}$$

where $P_{rel}(t)$ = the amount of sediment P released (in μgP/g sed) at time t.

P_r, P_s = the amount of sediment P released (in μgP/g sed) via the rapid and slow mechanisms, respectively.

and k_{rr}, k_{sr} = the first-order release rates for the rapid and slow mechanisms (in day^{-1}).

t = time (days).

A computer algorithm was developed to calculate the four release coefficients (P_r, P_s, k_{sr} and k_{rr}) from the bioassay data (values of P_{rel} versus t). Since many of the k_{rr} values obtained were comparable in magnitude to the bulk diffusion rate (α=2.065 day^{-1}) measured for the DCDA reactors, the rapid component (P_r) was assumed to be released instantly and Equation 11 was rewritten in the form:

$$P_{rel}(t) = P_r + P_s(1-e^{-k_{sr}t}) \tag{12}$$

The rate of sediment P release, W(t), is given by:

$$W(t) = m\,\frac{dP_{rel}}{dt} = m\,k_{sr}\,P_s\,e^{-k_{sr}t} \tag{E.1}$$

where m = the mass of sediments in the DCDA (g).

and $W(t)$ has units of μg/day.

If the soluble P concentration on the assay side of the DCDA is assumed to be maintained at zero by the P-starved algal culture, a mass balance for soluble P performed about the sediment side of the DCDA yields:

$$\frac{dC_1}{dt} = \frac{W(t)}{V} - \alpha C_1 \tag{E.2}$$

where C_1 = the soluble P concentration on the sediment side (μg/ℓ).

V = the volume of the sediment vessel (ℓ).

and α = the bulk diffusion coefficient for the DCDAs (day^{-1}).

or,

$$\frac{dC_1}{dt} + \alpha C_1 = \frac{m\ k_{sr}\ P_s}{V} e^{-k_{sr}t} \tag{E.3}$$

Setting $Q_1 = \frac{C_1 V}{m}$

where Q_1 = the quantity of P released from the sediments, but remaining in the sediment vessel (μgP/g sed).

results in the equation:

$$\frac{dQ_1}{dt} + \alpha Q_1 = k_{sr}\ P_s\ e^{-k_{sr}t} \tag{E.4}$$

This is a linear differential equation that may be solved by applying an integrating factor of $e^{\alpha t}$. The resulting solution is (Ross, 1974):

$$Q_1 = e^{-\alpha t}[\int e^{\alpha t}\, k_{sr}\, P_s\, e^{-k_{sr}t}\, dt + C] \quad (E.5)$$

where C = constant of integration.

Or,
$$Q_1 = e^{-\alpha t}[\int k_{sr}\, P_s\, e^{(\alpha - k_{sr})t}\, dt + C] \quad (E.6)$$

Performing the integration yields:

$$Q_1 = \frac{k_{sr}\, P_s}{(\alpha - k_{sr})}\, e^{-k_{sr}t} + C\, e^{-\alpha t} \quad (E.7)$$

Using the initial condition: $Q_1 = P_r$ at t=0 to solve for the integration constant gives

$$C = P_r - \frac{k_{sr}\, P_s}{(\alpha - k_{sr})} \quad (E.8)$$

Substituting this into Equation .7:

$$Q_1 = \frac{k_{sr}\, P_s}{(\alpha - k_{sr})}\, (e^{-k_{sr}t} - e^{-\alpha t}) + P_r\, e^{-\alpha t} \quad (E.9)$$

C_2 may be defined as the concentraiton (μgP/ℓ) of particulate P in the assay vessel attributable to release from the seidments (i.e., C_2 = total PP-initial PP at t=0). Assuming that soluble P is taken up immediately by the assay algae, a mass balance for C_2 about the assay vessel of the DCDA yields:

$$\frac{dC_2}{dt} = \alpha C_1 \quad (E.10)$$

Multiplying both sides by V/m and letting $Q_2 = VC_2/m$, where Q_2 = cumulative uptake of sediment P by algae (μgP/g sed):

$$\frac{dQ_2}{dt} = \alpha Q_1 = \alpha\left[\frac{k_{sr}\ P_s}{(\alpha-k_{sr})}\ (e^{-k_{sr}t} - e^{-\alpha t}) + P_r\ e^{-\alpha t}\right] \quad (E.11)$$

Integrating both sides:

$$Q_2 = \frac{-\alpha\ P_s}{(\alpha-k_{sr})}\ e^{-k_{sr}t} + \frac{k_{sr}\ P_s}{(\alpha-k_{sr})}\ e^{-\alpha t} - P_r\ e^{-\alpha t} + C \quad (E.12)$$

where C = constant of integration.

Since $C_2 = 0$ at t=0,

$$C = \frac{\alpha\ P_s}{(\alpha-k_{sr})} - \frac{k_{sr}\ P_s}{(\alpha-k_{sr})} + P_r \quad (E.13)$$

and, substituting into Equation E.12,

$$Q_2 = \frac{\alpha\ P_s}{(\alpha-k_{sr})}\ (1-e^{-k_{sr}t}) - \frac{k_{sr}\ P_s}{(\alpha-k_{sr})}\ (1-e^{-\alpha t}) + P_r(1-e^{-\alpha t}) \quad (E.14)$$

The computer algorithm used to calculate the two-component release coefficients sought to optimize the correlation between the measured values of Q_2 (from the bioassays) and the predicted values given by Equation E.14. The procedure involved an iterative search for the value of $P_{ult}(=P_r + P_s)$.

Since $P_{ult} = Q_2$ at $t=\infty$, from Equation E.14,

$$P_{ult} = \frac{\alpha\ P_s}{(\alpha-k_{sr})} - \frac{k_{sr}\ P_s}{(\alpha-k_{sr})} + P_r \quad (E.15)$$

and

$$(P_{ult}-Q_2) = \frac{\alpha\, P_s}{(\alpha-k_{sr})}\, e^{-k_{sr}t} - \frac{k_{sr}\, P_s}{(\alpha-k_{sr})}\, e^{-\alpha t} + P_r\, e^{-\alpha t} \quad (E.16)$$

If $\alpha >> k_{sr}$, at high values of t, $e^{-\alpha t} \approx 0$ and $\alpha/(\alpha-k_{sr}) \approx 1$, so

$$\ln(P_{ult}-Q_2) \approx \ln P_s - k_{sr}t \quad (E.17)$$

Therefore, if the early data points are eliminated from the bioassay data, a plot of $\ln(P_{ult}-Q_2)$ versus t should have a slope of $-k_{sr}$ and an intercept equal to $\ln P_s$. Then P_r can be obtained from the equation $P_r = P_{ult} - P_s$. A listing of the computer program used to execute these steps is also presented in this Appendix.

```
20  PX=0  : PY=0  : PZ=0  : KY=0  : KZ=0  : RX=0
30  PT=0  : P1=0  : P2=0  : K1=0  : K2=0  : R=0
40 DIM P(20),T(20),X(20),Y(20)
60 REM PHOSPHORUS AVAILABILITY KINETICS: ONE INSTANTANEOUS COMPONENT
65 REM     AND ONE SLOWER FIRST-ORDER COMPONENT.
70 REM READING IN INFORMATION THAT STAYS THE SAME FOR ALL SAMPLES
80 REM   CC = CONVERGENCE CRITERION (ACCEPTABLE INCREMENTAL INCREASE
85 REM          IN CORRELATION BETWEEN PREDICTED AND OBSERVED P UPTAKE)
90 REM   IGMIN = MINIMUM NUMBER OF POINTS TO BE IGNORED IN
100 REM          CALCULATING SLOW RELEASE COEFFICIENTS
110 REM  IGMAX = MAXIMUM NUMBER OF POINTS TO BE IGNORED
120 REM  NOSAM = NUMBER OF SAMPLES TO BE ANALYZED
125 REM  ALPHA = THE DIFFUSION COEFFICIENT FOR THE DCDA'S
130 READ CC,IGMIN,IGMAX,NOSAM,ALPHA
135 PRINT "INPUT DATA:  CC=";CC;"  IGMIN=";IGMIN;"  IGMAX=";IGMAX;
136 PRINT "  NOSAM=";NOSAM
140 REM OPENING UP A FILE TO STORE RESULTS
150 OPEN "O",#1,"INRELCO"
160 REM  PROGRAM WILL NOW READ IN DATA ON ONE SAMPLE AT A TIME,
170 REM   PERFORM CALCULATIONS, STORE THE RESULTS IN A FILE NAMED
180 REM   "INRELCO", AND GO ON TO THE NEXT SAMPLE.
190 FOR K = 1 TO NOSAM
200 REM  NS = SAMPLE I.D. NUMBER;  N = NUMBER OF DATA POINTS
210 READ NS,N
215 PRINT "VALUES READ IN:  NS=";NS;"  AND N=";N
220 FOR J = 1 TO N
223 REM READING IN TIME AND CUMULATIVE P RELEASE AT EACH SAMPLING:
230 READ T(J),P(J)
233 PRINT "TIME #";J;"=";T(J);"   P RELEASE =";P(J)
240 NEXT J
340 FOR M = IGMIN TO IGMAX
350 IT = 0
360 PX=0  : PY=0  : PZ=0  : KY=0  : KZ=0  : RX=0
370 PT=0  : P1=0  : P2=0  : K1=0  : K2=0  : R=0
380 PT = P(N) + 1
390 GOSUB 1140
400 IT = IT + 1
405 REM  GENERATING DATA FOR LINEAR REGRESSION TO FIND SLOW RELEASE
406 REM      COEFFICIENTS (P2 AND K2) AND ULTIMATE RELEASE (PT).
410 FOR I = M+1 TO N
420 Y(I) = LOG(PT - P(I))
430 X(I) = T(I)
440 GOSUB 1160
450 NEXT I
460 N = N - M
465 REM    NOW CALCULATING LINEAR REGRESSION COEFFICIENTS:
470 GOSUB 1220
480 N = N + M
495 REM  NOW CALCULATING SLOW RELEASE COEFFICIENTS (K2 AND P2):
500 REM  SLOW RELEASE RATE, K2 (PER DAY):
510 K2 = -1 * B1
520 REM  SIZE OF SLOWLY RELEASED COMPONENT, P2 (UG P/G SED):
530 P2 = EXP(B0)
540 REM  NOW CALCULATING THE SIZE OF THE RAPIDLY RELEASED COMPONENT,
545 REM      P1, IN UNITS OF UG P/G SED :
550 P1 = PT - P2
```

```
560 IF P1 <= 0 THEN GOTO 770
605 REM  NOW CHECKING CORRELATION BETWEEN OBSERVED AND
610 REM     PREDICTED RELEASE:
620 REM  DEFINING FUNCTIONS TO BE USED IN PREDICTING P UPTAKE ON THE
625 REM      ASSAY SIDE VERSUS TIME:
630 DEF FNP1(T) = ((ALPHA*P2)/(ALPHA-K2))*(1-EXP(-(K2*T)))
631 DEF FNP2(T) = ((K2*P2)/(ALPHA-K2))*(1-EXP(-(ALPHA*T)))
632 DEF FNP3(T) = P1*(1-EXP(-(ALPHA*T)))
640 GOSUB 1140
645 REM  CALCULATING THE PREDICTED CUMULATIVE UPTAKE OF P ON THE
648 REM     ASSAY SIDE FOR EACH SAMPLING DATE:
650 FOR I = 1 TO N
653 A = FNP1(T(I))
655 B = FNP2(T(I))
657 C = FNP3(T(I))
660 Y(I) = A - B - C
670 X(I) = P(I)
675 REM  DETERMINING CORRELATION COEFFICIENT (R) BETWEEN
677 REM     PREDICTED (Y) AND OBSERVED (X) UPTAKE:
680 GOSUB 1160
690 NEXT I
700 GOSUB 1220
740 REM  LIMITING THE MAXIMUM NUMBER OF ITERATIONS TO 100:
745 IF IT = 100 THEN GOTO 790
747 REM  CHECKING TO SEE IF CONVERGENCE CRITERION HAS BEEN MET.
748 REM     IF NOT, PT IS INCREASED BY 1 AND ROUTINE CONTINUED:
750 IF (R - RX) < CC THEN GOTO 790
760 PX=PT : PY=P1 : PZ=P2 : KY=K1 : KZ=K2 : RX=R
770 PT = PT + 1
780 GOTO 390
790 PT=PX : P1=PY : P2=PZ : K1=KY : K2=KZ : R=RX
795 REM   COPYING RESULTS TO DISK:
800 PRINT#1,NS;M;IT;PT;P1;P2;K2;R
810 NEXT M
820 NEXT K
830 CLOSE
840 END
1120 REM  THIS IS THE LINEAR REGRESSION PORTION OF THE PROGRAM:
1140 XX = 0 : YY = 0 : X2 = 0 : Y2 = 0 : XY = 0
1150 RETURN
1160 XX = XX + X(I)
1170 YY = YY + Y(I)
1180 X2 = X2 + X(I)^2
1190 Y2 = Y2 + Y(I)^2
1200 XY = XY + X(I) * Y(I)
1210 RETURN
1220 SX = (X2 - XX^2 / N) / (N - 1)
1230 SY = (Y2 - YY^2 / N) / (N - 1)
1240 SP = (XY - XX * YY / N) / (N - 1)
1250 B1 = SP/SX
1260 B0 = (YY - B1 * XX) / N
1265 V = B1/ABS(B1)
1270 R = (B1 / ABS(B1)) * SQR(SP ^ 2 / (SX * SY))
1280 RETURN
1290 END
```